A Radio Frequency Quadrupole Instrument for use with Accelerator Mass Spectrometry: Application to Low Kinetic Energy Reactive Isobar Suppression and Gas–Phase Anion Reaction Studies

by

John Alexander Eliades

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy

Department of Geology (home)
Department of Physics (collaborative programme)
University of Toronto

© Copyright by John Alexander Eliades 2012
A radio frequency (rf) quadrupole instrument, currently known as an Isobar Separator for Anions (ISA), has been integrated into an Accelerator Mass Spectrometry (AMS) system to facilitate anion–gas reactions before the tandem accelerator. An AMS Cs⁺ sputter source provided ≥ 15 keV ions that were decelerated in the prototype ISA to < 20 eV for reaction in a single collision cell and re-accelerated for AMS analysis. Reaction based isobar suppression capabilities were assessed for smaller AMS systems and a new technique for gas–phase reaction studies was developed.

Isobar suppression of $^{36}\text{S}^-$ and $^{12}\text{C}_3^-$ for $^{36}\text{Cl}$ analysis, and YF$_3^-$ and ZrF$_3^-$ for $^{90}\text{Sr}$ analysis were studied in NO$_2$ with deceleration to ≤ 12 eV. Observed attenuation cross sections, $\sigma$ [x 10$^{-15}$ cm$^2$], were $\sigma$(S$^-$ + NO$_2$) = 6.6, $\sigma$(C$_3^-$ + NO$_2$) = 4.2, $\sigma$(YF$_3^-$ + NO$_2$) = 7.6, $\sigma$(ZrF$_3^-$ + NO$_2$) = 19. With 8 mTorr NO$_2$, relative attenuations of S$^-$/Cl$^-$ ~ 10$^{-6}$, C$_3^-$/Cl$^-$ ~ 10$^{-7}$, YF$_3^-$/SrF$_3^-$ ~ 5 x 10$^{-5}$ and ZrF$_3^-$/SrF$_3^-$ ~ 4 x 10$^{-6}$ were observed with Cl$^-$ ~ 30% and SrF$_3^-$ > 90% transmission. Current isobar attenuation limits with ≤ 1.75 MV accelerator terminal voltage and ppm impurity levels were calculated to be $^{36}\text{S}^-$/Cl$^-$ ~ 4 x 10$^{-16}$, $^{12}\text{C}_3^-$/Cl$^-$ ~ 1.2 x 10$^{-16}$, $^{90}\text{YF}_3^-$/SrF$_3^-$ ~ 10$^{-15}$ and $^{90}\text{ZrF}_3^-$/SrF$_3^-$ ~ 10$^{-16}$.
Using 1.75 MV, four $^{36}$Cl reference standards in the range $4 \times 10^{-13} \leq {^{36}\text{Cl}/\text{Cl}} \leq 4 \times 10^{-11}$ were analyzed with 8 mTorr NO$_2$. The measured $^{36}\text{Cl}/\text{Cl}$ ratios plotted very well against the accepted values. A sample impurity content S/Cl $\leq 6 \times 10^{-5}$ was measured and a background level of $^{36}\text{S}^-/\text{Cl} \leq 9 \times 10^{-15}$ was determined.

Useful currents of a wide variety of anions are produced in AMS sputter sources and molecules can be identified relatively unambiguously by stripping fragments from tandem accelerators. Reactions involving YF$_3^-$, ZrF$_3^-$, S$^-$ and SO$^- +$ NO$_2$ in the ISA analyzed by AMS are described, and some interesting reactants are identified.
— ὁ ἄναξ οὗ τὸ μαντεῖόν ἐστι τὸ ἐν Δελφοῖς οὔτε λέγει οὔτε κρύπτει ἀλλὰ σημαίνει.
— φύσις κρύπτεσθαι φιλεῖ.
— χρυσὸν οἱ διζήμενοι γην πολλὴν ὀρύσσουσι καὶ εὑρίσκουσιν ὀλίγον.
— εάν μὴ ἐλπιῆται ἀνέλπιστον οὐκ ἔξευρήσει, ἀνεξετεύνητον ἐὸν καὶ ἀπορον.
— κακοὶ μάρτυρες ἀνθρώποισιν ὀφθαλμοὶ καὶ οὖτα βαρβάρους ψυχὰς ἔχοντων

— The lord whose oracle is in Delphi neither declares nor conceals, but gives a sign.
— Nature loves to hide.
— Seekers of gold dig up much earth and find little.
— He who does not expect will not find out the unexpected, for it is trackless and unexplored.
— Eyes and ears are poor witnesses for men if their souls do not understand the language.

Ἡράκλειτος (Heraclitus), c. the sixty-ninth Olympiad (504-501 BCE) ¹

— 无名人曰：”汝游心于淡，合气于漠，顺物自然而无容私焉，而天下治矣.”
— 无为名尸，无为谋府，无为事任，无为知主。休尽无穷，而游无朕。尽其所受于天，而无见得，亦虚而已！至人之用心若镜，不将不迎，应而不藏，故能胜物而不伤。
— The nameless sage said, “Let your mind wander in pure nature, remain inactive, follow the natural course of events, and leave your personal will aside. In this way the world will be governed.”
— Sever yourself from fame and do away with schemes. Shun worldly burdens and keep away from wisdom. Experience the bounteous Tao and wander in the realm of infinity. Enjoy what nature has endowed you with and do not think that you have gained anything – everything is of nihility. The perfect man has a mind like a mirror, which neither welcomes nor sends, which reflects things but does not retain things. Therefore, he can act successfully without wearing out his mind.

莊子 (庄子, Zhuangzi), c. 369 – 286 BCE during the Chinese period of Warring States (战国中期) ²

“…It is not the duty or place of a philosopher to dictate belief, and all hypothesis is more or less matter of belief; he has but to give his facts and his conclusions, and so much of the logic which connects the former with the latter as he may think necessary, and then to commit the whole to the scientific world for present, and, as he may sometimes without presumption believe, for future judgement.”

From Professor M. Faraday to Professor P. Riess (Faraday and Riess 1856 p.1)

¹ Fragments XXXIII, VIII, X, VII and translation: Kahn 1979, p. 42, 32, 30, 30, 34 (Freeman 1946, p. 104)
² Passages and translation: Wang et. al. 1997, p. 136, 144
Acknowledgements

I am greatly indebted to the group at IsoTrace Laboratory (Toronto, Ontario, Canada) for allowing me to use the facilities and for the opportunity to participate in their projects. In particular, I am grateful to University of Toronto Prof. Emeritus A.E. Litherland for so many stimulating and educational discussions, and his help, guidance and encouragement. His love of physics and science, and seemingly infinite supply of energy had a profound influence on me. For taking me under his wing, training me on the system, helping with several experiments and technical difficulties, providing so many insights on science and beyond, and generally befriending me, I thank Dr. X.–L. Zhao. The technical expertise and experience of Prof. W.E. Kieser was invaluable. Also, his guidance on writing grant proposals and making presentations, and help with administrative matters are greatly appreciated.

Besides those I worked with, I thank the former members of IsoTrace, especially Dr. J. P. Doupé and Dr. I. Thomsky, for their instrumental roles in conceiving the Isobar Separator for Anions (ISA). I also thank those at IONICS Mass Spectrometry Group Inc. (Bolton, Ontario, Canada), particularly Dr. G. Javahery, Dr. L. Cousins and Dr. I. Thomsky, for designing and producing the original ISA and helping with technical difficulties.

My deepest gratitude goes to Prof. D. W. Davis. He hired me as a summer research assistant while I was an undergraduate student, suggested this project and introduced me to the group at IsoTrace, acted as a co-supervisor and generally encouraged and supported me. My thanks also go to Chris Charles for his friendship and insights into Earth Science as he conducted his graduate studies with Prof. Davis while I was at IsoTrace. To both of you, I owe very much.

I thank University of Toronto for extending funding to IsoTrace so that experimental work could be finished, and to University of Ottawa for supporting the laboratory thereafter, during difficult economic times. I am also grateful for funding from Professors Litherland and Kieser, Department of Geology, Government of Ontario, Government of Canada (as part of the initial grant for this project) and Prof. J. Cornett (University of Ottawa). Thank you also to Ms. L. Slotkin, Department of Geology graduate coordinator, for helping keep me on track and general administrative assistance.

Finally, eternal thanks to my family and friends. I cannot express enough gratitude to my parents.
# Table of Contents

Partial List of Equations and Colour Format ........................................................................ xvi

1 Introduction ................................................................................................................................... 1—1  
1.1 Guide to the Thesis ................................................................................................................. 1—2

2 Background ................................................................................................................................ 2—4  
2.1 Mass ........................................................................................................................................ 2—4  
2.2 Mass Spectrometry and Filters ............................................................................................. 2—5  
2.3 Trace Isotope Abundance Measurements ............................................................................ 2—10  
2.4 Mass Spectrometry with Tandem Electrostatic Accelerators ................................................ 2—13  
2.5 Some Recent and Related Technical Advances for Lower Kinetic Energy Analyses ................... 2—15

3 RF Quadrupole Collision Cells – A Historical Context for the ISA ........................................ 3—19  
3.1 RF-Multipole Collision Cells as Chemical Isobar Filters and Ion Coolers .......................... 3—20  
3.2 General and Technical References ....................................................................................... 3—21

4 Ion Motion in RF Quadrupole Fields ...................................................................................... 4—23  
4.1 Basic Equations of Ion Motion in an Ideal Field .................................................................... 4—25  
4.1.1 Stability parameters in an ideal quadrupole field ............................................................ 4—28  
4.1.2 The Effective Potential V* and RF-Heating ................................................................. 4—32

5 Ion Trajectory Simulations in Ideal RF Quadrupole Fields .................................................... 5—36  
5.1 A Matrix Approximation for Trajectory Analysis ............................................................... 5—36  
5.2 Ion Trajectory Simulation Procedure ................................................................................... 5—38  
5.2.1 Evaluation of Trajectory Simulation Time-Step ............................................................. 5—39

5.3 General rf Quadrupole Ion Guide Ion Trajectory Characteristics ....................................... 5—45  
5.3.1 General Properties ............................................................................................................ 5—45  
5.3.2 Oscillation Frequency and Period .................................................................................... 5—48  
5.3.3 Initial Position and Kinetic Energy ................................................................................... 5—49  
5.3.4 Initial rf Phase ................................................................................................................ 5—55  
5.3.5 Initial Direction of Ion Motion – Converging vs. Diverging Motion ............................... 5—59  
5.3.6 Initial Radial Velocity Direction vs. Initial rf Phase ..................................................... 5—60  
5.3.7 General Discussion: Implications for Ion Transmission ................................................ 5—65
5.4 Multiple rf Segments in Series

5.4.1 RF Quadrupole Segments with Spatial Offsets

5.4.2 Varying $V_{0p}$ and $\omega$ While Maintaining Constant $q_2$

5.4.3 Apertures and ‘$q_2$ focussing’

5.4.3.1 Calculation Procedure and Initial Conditions

5.4.3.2 Transmission through Apertures and ‘$q_2$ Focussing’

5.4.3.3 Conclusions

6 Ion-Gas Interactions

6.1 Kinetic Energy Transfer and Conversion

6.2 Cross Sections, Polarizability and Interaction Probability

6.3 Reaction Energy and Barriers

6.3.1 Application to the Oak Ridge RF Quadrupole Isobar Separator

6.4 Some Notes on Cooling Gas Selection

7 Experimental System

7.1 Test Bed Vacuum System and Pressure Monitoring

7.2 Deck High Voltage Measurement ($V_s$, $V_{ISA}$ and $\Delta V_{ISAS}$)

7.2.1 Resistor Circuit Calibration and Measurement Uncertainties

7.3 Ion Flux Measurements

7.4 Description of the Isobar Separator for Anions

7.5 Sputter Target Material, Cs and Gas Manufacturer Information

7.5.1 NO$_2$/N$_2$O$_4$ Equilibrium Ratio

7.6 Typical Settings

7.7 Stripping Yield vs. Accelerator Terminal Voltage Correction

8 ISA Vacuum Transmission and $q_2$ Focussing

8.1.1 Transmission vs. Transverse Ion Kinetic Energy

8.1.2 Transmission vs. RF2 $V_{pp}$ at Fixed $\Delta V_{ISAS}$ – ‘$q_2$ Focussing’

8.1.3 Large Aperture Transmission

8.1.4 Transmission vs. RF1 and RF2 $V_{pp}$ through Tuned ISA

9 General Transmission in CH$_4$ and Ar

9.1 Molecular and Atomic Properties

9.2 Cooling in CH$_4$ and Ar

9.2.1 Discussion
9.3 ISA Transmission for Various Anions in CH₄ and Ar, and Cl⁻ and CN⁻ in NO₂ ................................................................. 9—146

9.3.1 Observed Trends in Anion Losses with CH₄, Ar and NO₂ .......... 9—147

10 C₃⁻, Cl⁻, S⁻ and SO⁻ Attenuations and Reactions with Gases: RF Quadrupole Accelerator Mass Spectrometry for the Study of Gas-Phase Anion Reactions ........ 10—152

10.1 Cl⁻ + Air, Ar, CH₄ and NO₂ ................................................................. 10—154

10.1.1 Preliminary Investigation of Potential Reactive Losses for Cl⁻ with Ar and NO₂ ................................................................. 10—157

10.1.2 Losses from Residual Gas ................................................................. 10—160

10.2 S⁻ + CH₄, Ar, N₂O, NO₂ and O₂: General Transmission .......... 10—161

10.3 S⁻ and SO⁻ + Ar, N₂O, NO₂ and O₂ ......................................................... 10—164

10.3.1 A Note on Reaction Product Transmissions with Reactant ISA Tuning .... 10—167

10.3.2 Molecular Identification from Stripping Fragments and NSO₂ – ................. 10—167

10.3.3 S⁻ and SO⁻ + N₂O ........................................................................ 10—170

10.3.4 S⁻ and SO⁻ + O₂ ........................................................................ 10—173

10.3.5 S⁻ and SO⁻ + NO₂ and Ar ................................................................. 10—176

10.3.5.1 Fast Neutral / Ion Contribution to the S⁻ + NO₂ Plateau .......... 10—177

10.3.5.2 S⁻ and SO⁻ + NO₂ Reactions ......................................................... 10—183

10.3.6 A Note on Sputtered Anion Beam Energy Distributions .......... 10—189

10.4 ¹²C₃⁻ + Ar and NO₂ ................................................................. 10—191

10.5 Reaction and Total Attenuation Cross Section Estimates ............... 10—194

10.6 Summary and Conclusions ................................................................. 10—197

11 ³⁶Cl Reference Standards Comparison ................................................................. 11—201

11.1 ³⁶Cl/Cl = 4 x 10⁻¹¹ Measurement at V₇ = 1.75 MV vs. NO₂ Pressure: A test of the ³⁶Cl⁺³ blank ................................................................. 11—201

11.1.1 Background ............................................................................... 11—202

11.1.2 Results ..................................................................................... 11—203

11.2 ³⁶Cl Reference Material Measurements ......................................................... 11—205

11.2.1 Background ............................................................................... 11—205

11.2.2 Results ..................................................................................... 11—207

11.3 Discussion ..................................................................................... 11—208

12 Isobar Suppression for ⁹⁰Sr Analyses: SrF₅⁻, YF₃⁻ and ZrF₃⁻ + NO₂ Attenuations and Reactions ................................................................. 12—213
12.1 SrF$_3^-$, YF$_3^-$, ZrF$_3^-$ + NO$_2$ Attenuations ............................................................... 12—213
12.2 ZrF$_3^-$ + NO$_2$ Reaction Channels ......................................................................... 12—215
12.3 YF$_3^-$ + NO$_2$ Reaction Channels .......................................................................... 12—218
12.4 Cross Section Estimates .............................................................................................. 12—219
12.5 Discussion ........................................................................................................... 12—220

13 Summary and Conclusions ..................................................................................... 13—222
13.1 Isobar Suppression .............................................................................................. 13—222
  13.1.1 Application to $^{36}$Cl ...................................................................................... 13—223
  13.1.2 Application to Sr and Cs ............................................................................. 13—224
13.2 Gas–Phase Anion Reaction Studies ..................................................................... 13—225
13.3 Future Development ............................................................................................ 13—227
13.4 Concluding Remarks ........................................................................................... 13—229

References ...................................................................................................................... 230
Software References ........................................................................................................ 241
APPENDIX A ............................................................................................................................. 242
  A.I Summary (‘Cheat-Sheets’)................................................................................... 242
  A.II Pressure Conversions ....................................................................................... 244
  A.III Mass Conversions ............................................................................................. 245
  A.IV Energy Conversions ......................................................................................... 245
  A.V Non-Relativistic Kinetic Energy in Non-SI units ............................................... 246

APPENDIX B ............................................................................................................................. 247
  B.I Summary ..................................................................................................................... 247
  B.II Decay Constant Variability .................................................................................. 248
  B.III Basic Decay Equations ....................................................................................... 249

APPENDIX C ............................................................................................................................. 254
  C.I Summary ..................................................................................................................... 254
  C.II Beta-decay and Electron Capture .................................................................... 254

APPENDIX D ............................................................................................................................. 259
  Mass and Isobar $\Delta$M Equations and Table ............................................................. 259
List of Figures

Figure 2-1: AMS System Layout Based on the IsoTrace Laboratory Heavy Element Line .. 2—14
Figure 4-1: Sketch of a General Cylindrical rf Quadrupole Instrument ................................. 4—24
Figure 4-2: Illustration of the Potential Offsets for an rf Quadrupole Instrument .................. 4—30
Figure 4-3: Effective Potential $V'(r)$ for $n = 2, 3, 4$ and $5$ ...................................................... 4—35
Figure 5-1: Trajectory Simulation Plots $X(t)$ v. t and $Y(t)$ v. t for $0.1 < q_2 < 0.5$ for an Ideal rf-Quadrupole Field (see p. 5—40 for caption) ....................................................... 5—41
Figure 5-2: Trajectory Simulation Plots $X(t)$ v. t and $Y(t)$ v. t for $0.55 < q_2 < 0.9$ for an Ideal rf-Quadrupole Field (see p. 5—40 for caption) ........................................................ 5—42
Figure 5-3: 2-D Projections of Trajectory Position $X(t)$ v. $Y(t)$ for $0.1 < q_2 < 0.9$ for an Ideal rf Quadrupole Field (see p. 5—48 for caption) ......................................................... 5—46
Figure 5-4: Relative Scale of 2-D Trajectory Projections for $X(t)$ vs. $Y(t)$ ......................... 5—47
Figure 5-5: Small Oscillations for X-Motion $0.10 < q_2 < 0.20$ – Low $q_2$ ‘Wiggle’ Motion... 5—50
Figure 5-6: Expanded View of a Stable $q_2 = 0.90$ Trajectory............................................... 5—51
Figure 5-7: Influence of Initial Position and Kinetic Energy on Trajectory Amplitude........ 5—52
Figure 5-8: Comparison of Two Initial Positions on Trajectory Amplitude for $0.1 < q_2 < 0.5$ .......................................................................................................................... 5—53
Figure 5-9: Comparison of Two Initial Positions on Trajectory Amplitude for $0.55 < q_2 < 0.9$ ........................................................................................................................ 5—54
Figure 5-10: Influence of Initial rf Phase on Trajectory Amplitude for 2 Initial Positions .... 5—56
Figure 5-11: Maximum Effective Potential Experienced in x, y and r Coordinates vs. Initial rf Phase ...................................................................................................................... 5—57
Figure 5-12: Maximum Effective Potential vs. Initial rf Phase for Various $q_2$ and $K_r(0)$ ...... 5—58
Figure 5-13: Effect of Initial Velocity Direction on Trajectory Amplitude and Peak Positions I ................................................................................................................................ 5—59
Figure 5-14: Effect of Initial Velocity Direction on Trajectory Amplitude and Peak Position II ................................................................................................................................ 5—61
Figure 5-15: Influence of Initial rf Phase and Initial Ion Velocity Direction on Maximum and Minimum Amplitude Trajectories ................................................................ 5—62
Figure 5-16: Maximum Effective Potential vs. Initial rf Phase and Initial Ion Velocity Direction................................................................................................................... 5—63
Figure 5-17: Influence of Initial rf Phase and Initial Ion Velocity Direction on Ion Trajectories ........................................................................................................................................ 5—64
Figure 5-18: 2-D Trajectory Projections, Y(t) vs. X(t), for Varied Initial rf Phases and Initial Ion Velocity Directions ........................................................................................................................................ 5—65
Figure 5-19: Ion Trajectories with rf Quadrupole Cell Position Offsets ........................................................................................................................................ 5—68
Figure 5-20: Amplitude Increase for a Frequency Offset $\omega' = 2\omega$ at $Ln_{rf} = 24$ for $q_2 = 0.2$ and $K_{x,y}(0) = 0.5\text{eV}$ ........................................................................................................................................ 5—72
Figure 5-21: Amplitude Increases and Decreases for a Frequency Offset $\omega' = 2\omega$ at $Ln_{rf} = 25.5$ for $q_2 = 0.2$ and $K_{x,y}(0) = 1\text{eV}$ ........................................................................................................................................ 5—73
Figure 5-22: Amplitude Decrease for a Frequency Offset $\omega' = 2\omega$ at $Ln_{rf} = 27$ for $q_2 = 0.2$ and $K_{x,y}(0) = 1\text{eV}$ ........................................................................................................................................ 5—74
Figure 5-23: Amplitude Changes for a Frequency Offset $\omega' = \omega/2$ at $Ln_{rf} = 24$ for $q_2 = 0.2$ and $K_{x,y}(0) = 0.5\text{eV}$ ........................................................................................................................................ 5—75
Figure 5-24: Amplitude Changes for a Frequency Offset $\omega' = \omega/2$ at $Ln_{rf} = 25.5$ for $q_2 = 0.2$ and $K_{x,y}(0) = 1\text{eV}$ ........................................................................................................................................ 5—76
Figure 5-25: Amplitude Increase for a Frequency Offset $\omega' = \omega/2$ at $Ln_{rf} = 27$ for $q_2 = 0.2$ and $K_{x,y}(0) = 0.025\text{eV}$ (thermal) ........................................................................................................................................ 5—77
Figure 5-26: Transmission With an Aperture Versus Without ........................................................................................................................................ 5—80
Figure 5-27: ‘$q_2$ Focusing’ for $K_{x,y}(0) = 1\text{eV}$ and 1 Aperture ........................................................................................................................................ 5—83
Figure 5-28: ‘$q_2$ Focusing’ for $K_{x,y}(0) = 0.5\text{eV}$ and 1 Aperture ........................................................................................................................................ 5—84
Figure 5-29: Transmission Through Two Apertures ........................................................................................................................................ 5—87
Figure 5-30: Transmission Through Three Apertures ........................................................................................................................................ 5—88
Figure 6-1: Laboratory and Centre of Mass Frames of Reference ........................................................................................................................................ 6—90
Figure 6-2: Transmission vs. Threshold for Electron Detachment for Oak Ridge rf Quadrupole Cooling Instrument ........................................................................................................................................ 6—105
Figure 6-3: Hard Sphere Elastic $\Delta K$ and $K_R$ vs. Mass Ratio of Projectile and Target ........................................................................................................................................ 6—107
Figure 7-1: Schematic Drawing of the ISA Test Bed and AMS System at IsoTrace Laboratory ........................................................................................................................................ 7—108
Figure 7-2: ‘Step-down’ Resistor Circuit and Multimeter Information ........................................................................................................................................ 7—111
Figure 7-3: Gas Ionization Detector Schematic ........................................................................................................................................ 7—115
Figure 7-4: Schematic Representation of the ISA Through 1 Plane ..................................... 7—116
Figure 7-5: Collision Cell Quadrupole Rod and Gradient Bar Offset Dimensions .......... 7—117
Figure 7-6: rf Quadrupole Rod Electrical Circuit Schematic ............................................... 7—118
Figure 7-7: Cl\(^{-} \rightarrow\) Cl\(^{+3}\) Equilibrium State Stripping Yields from References and
Comparison to Measured\(^{32}\)S\(^{-} \rightarrow\) \(^{32}\)S\(^{+3}\) Relative Intensities ........................................... 7—123
Figure 7-8: \(^{32}\)S\(^{-} \rightarrow\) \(^{32}\)S\(^{+3}\) Stripping Data and Curve Fits for Stripping Yield Corrections .... 7—125
Figure 8-1: Transmission vs. ISA Deck Voltage with and without ISA rf and DC ............. 8—128
Figure 8-2: Transmission vs. ISA RF2 V\(_{pp}\) – ‘q\(_2\) Focusing’ Peaks........................................... 8—130
Figure 8-3: Transmission vs. ISA RF1 and RF2 ................................................................... 8—136
Figure 9-1: Hard Sphere Elastic Collision Kinetic Energy Loss vs. Lab Frame
Scattering Angle for Cl\(^{-}\) on Ar and CH\(_{4}\) ............................................................................ 9—141
Figure 9-2: Expected Number of Collisions vs. ISA Collision Cell Pressure for Cl on Ar.. 9—143
Figure 9-3: Average Kinetic Energy vs. Number of Collisions and Average Number of
Collisions Required for Thermalization for K\(_{0}\) = 15 eV ......................................................... 9—144
Figure 9-4: Average Kinetic Energy vs. Number of Collisions and Average Number of
Collisions Required for Thermalization for K\(_{0}\) = 5 eV .......................................................... 9—145
Figure 9-5: Anion Attenuations in the ISA with 6 mTorr CH\(_{4}\), NO\(_{2}\) and Ar .................. 9—151
Figure 10-1: Representative \(^{35}\)Cl\(^{-}\) Transmissions through Ar, Air, CH\(_{4}\) and NO\(_{2}\) with .... 10—154
Figure 10-2: Cl\(^{-}\) + NO\(_{2}\) \(\rightarrow\) ClO\(^{-}\) Production with \(\Delta V_{ISAS} = 6.7\) V .............................................. 10—158
Figure 10-3: S\(^{-}\) Transmission in Ar, CH\(_{4}\), N\(_{2}\)O, NO\(_{2}\) and O\(_{2}\) vs. Pressure with
\(\Delta V_{ISAS} = 5 – 6.6\) V .............................................................................................. 10—162
Figure 10-4: Scan of the \(^{32}\)S\(^{-}\) Reaction Products from \(^{32}\)S\(^{-} +\) N\(_{2}\)O, NO\(_{2}\) and O\(_{2}\) with
\(\Delta V_{ISAS} = 4.8\) V to 6.3 V using the full AMS System to Detect the \(^{32}\)S\(^{+3}\) Fragment after
Stripping (caption on p. 10—159) .................................................................................... 10—166
Figure 10-5: Ionization Detector Channel Spectrum for NSO\(_{2}\)^{–} \(\rightarrow\) \(^{32}\)S\(^{+2}\) / \(^{16}\)O\(^{+1}\) .......... 10—169
Figure 10-6: S\(^{-}\) + N\(_{2}\)O Transmission and Reaction Products vs. Pressure at
\(\Delta V_{ISAS} = 6.6\) V ........................................................................................................ 10—171
Figure 10-7: S\(^{-}\) and SO\(^{-}\) + O\(_{2}\) Transmission and Reaction Products at \(\Delta V_{ISAS} = 4.8\) V .... 10—173
Figure 10-8: S\(^{-}\) + NO\(_{2}\) Attenuation Comparison for the ISA Over 3 Years
\(4.5 V < \Delta V_{ISAS} < 12.0\) V ...................................................................................... 10—178
Figure 10-9: S\textsuperscript{−} vs. NO\textsubscript{2} Attenuation with $\Delta V_{\text{ISAS}} = 5.3$ V and $-227$ V Detecting S$^+$ and S$^{+3}$ ........................................................................................................................................ 10—182

Figure 10-10: S\textsuperscript{−} and SO\textsuperscript{−} + NO\textsubscript{2} and Ar Transmission and Reaction Products with $\Delta V_{\text{ISAS}} < 7$ V ........................................................................................................................................ 10—186

Figure 10-11: $^{12}$C\textsubscript{3}\textsuperscript{−} + Ar and NO\textsubscript{2} Attenuations and Ionization Detector Spectra for $^{12}$C$^+$ ...................................................................................................................................... 10—192

Figure 11-1: $^{36}$Cl/Cl $\sim 4 \times 10^{-11}$ Reference Standard Measured at $V_T = 1.75$ MV vs. NO\textsubscript{2} Pressure ....................................................................................................................................... 11—204

Figure 11-2: Four $^{36}$Cl/Cl Reference Standard Ratios Measured at 1.75 MV with the ISA Compared to the Reference Values from PRIME Lab .................................................................................. 11—210

Figure 12-1: SrF\textsubscript{3}\textsuperscript{−}, YF\textsubscript{3}\textsuperscript{−} and ZrF\textsubscript{3}\textsuperscript{−} Relative Total Attenuations in NO\textsubscript{2} with $\Delta V_{\text{ISAS}} < 5.5$ V .................................................................................................................................... 12—215

Figure 12-2: ZrF\textsubscript{3}\textsuperscript{−} + NO\textsubscript{2} Reaction Channels with $\Delta V_{\text{ISAS}} = 4.8$ V .................................................................................................................. 12—217

Figure 12-3: $^{89}$YF\textsubscript{3}\textsuperscript{−} + NO\textsubscript{2} Reaction Channels with $\Delta V_{\text{ISAS}} = 5.3$ V .................................................................................................. 12—219
List of Tables

Table 2.1: Common Acceleration-Based Filters in Mass Spectrometry ................................... 2—7
Table 2.2: Typical Performance of Mass Spectrometers used in Biological and Petroleum Analyses* ................................................................................................................. 2—9
Table 5.1: Global Simulation Values ...................................................................................... 5—39
Table 5.2: Evaluation of Time Step $\Delta t$ for NumSteps = 1000 (for $\omega$) .................... 5—43
Table 5.3: Evaluation of Time Step $\Delta t$ for NumSteps = 1000 (for 2$\omega$) ..................... 5—44
Table 5.4: Measured vs. Calculated Major Periods for Low $q_2$ Trajectories .................. 5—49
Table 5.5: ‘$q_2$-Focus Values’ for Transmission Maxima through Apertures at $\text{Ln}_{\text{rf}}$ (Eq 5.15) .......................................................................................................................... 5—81
Table 6.1: Two-Particle Head-on Elastic Collision .............................................................. 6—91
Table 6.2: Two-Particle Head-on Elastic Collision with one Particle Initially at Rest .......... 6—91
Table 6.3: CM – Lab Frame Conversions for Elastic Scattering with one Particle Initially at Rest ........................................................................................................................ 6—95
Table 6.4: Transmission Data from Oak Ridge rf Quadrupole Cooling Instrument .......... 6—104
Table 6.5: Transmission Data from Oak Ridge using Threshold Electron Detachment Energy for $T_e$ Calculation ........................................................................................................ 6—104
Table 6.6: Estimated Electron Detachment Threshold Energies of $^{32}\text{S}^-$, $^{58}\text{Ni}^-$, $^{59}\text{Co}^-$ and $^{64}\text{Cu}^-$ on He .................................................................................................................... 6—105
Table 7.1: Meters for Experimental Measurements .............................................................. 7—114
Table 7.2: Typical Slit Openings (mm) ................................................................................ 7—121
Table 7.3: Typical AMS Settings for $X^- \to X^{+3}$ ................................................................ 7—121
Table 8.1: Transmission (FC2 to FC3) Results with L3 and L4 Removed ......................... 8—132
Table 8.2: ISA Settings for Transmission Studies with L3 and L4 Removed ...................... 8—132
Table 8.3: Transmission (FC2 to FC3) Results with $L2 = L3 = \phi 3\text{ mm and L4 Removed}$. ............................................................................................................................... 8—133
Table 8.4: ISA Settings for Transmission Studies with $L2 = L3 = \phi 3\text{ mm and L4 Removed}$............................................................................................................................... 8—133
Table 9.1: Molecular Structure, Bond Lengths and Bond Dissociation Energies for N₂O, NO₂, CH₄, O₃, O₂ and N₂............................................................................................................................. 9—138
Table 9.2: Electron Binding and Dipole Properties for N₂O, NO₂, CH₄, O₃, O₂ and N₂............................................................................................................................. 9—139
Table 9.3: Atomic Radius, Electron Binding and Polarizability for Ar, C, Cl, H, N, O and S...................................................................................................................................... 9—139
Table 9.4: Transmission Data for Various Anions in Ar, NO₂ and CH₄........................................ 9—148
Table 10.1: Representative ISA Settings for Figure 10-1 and Figure 10-2 ................................. 10—155
Table 10.2: Representative ISA Settings for S⁻ Attenuation Studies .................................... 10—161
Table 10.3: Sputter, Kinetic Energy and Transmission Data for S⁻ and SO⁻ on Ar, CH₄, N₂O, NO₂ and O₂ .................................................................................................................................. 10—163
Table 10.4: Threshold Energy Estimates for Selected S⁻ + N₂O Reactions .............................. 10—171
Table 10.5: Threshold Energy Estimates for Selected S⁻, SO⁻ and SO₂⁻ + O₂ Reactions............ 10—174
Table 10.6: Base Pressure S⁻ Signal vs. ΔVISAS: Support for Fast Neutrals and Fast Ions .............................................................................................................................. 10—179
Table 10.7: Threshold Energy Estimates for Selected S⁻, SO⁻, SO₂⁻ and NO₂⁻ + NO₂ Reactions............................................................................................................................. 10—184
Table 10.8: Cross Section and Reaction Rate Coefficient Estimates for C₃⁻, S⁻, SO⁻, NO₂⁻ + NO₂, O₂ .................................................................................................................................. 10—200
Table 11.1: Targets used for ³⁶Cl Reference Standard Measurements .................................... 11—201
Table 11.2: Raw Data from ³⁶Cl Reference Standard Measurements ..................................... 11—211
Table 11.3: ³⁶Cl/Cl Measured Ratios .................................................................................... 11—212
Table 12.1: Sputter, Kinetic Energy and Transmission Data for SrF₃⁻, YF₃⁻ and ZrF₅⁻ in NO₂.......................................................................................................................... 12—214
Table 12.2: ZrF₅⁻ + NO₂ Reaction Channels with ΔVISAS = 5.3 V........................................... 12—218
Table 12.3: Attenuation Cross Section Estimates for YF₃⁻ and ZrF₅⁻ in NO₂.............. 12—220
### Partial List of Equations and Colour Format

Headings are given in **blue** and references (eg to pages, equations and figures) written in **purple** are linked to the source in ‘pdf’ and ‘Word’ documents. The reader may need to hold <ctrl (♦)> when ‘clicking’, and it is advisable to remember the page from which you navigated away.

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>deck offset voltage</strong>&lt;br&gt;Eq 7.1 p. 7—109</td>
<td>$\Delta V_{ISA} = V_{ISA} - V_S$&lt;br&gt;The difference between the ISA ($V_{ISA}$) and ion source ($V_s$) deck voltages (ISA deceleration voltage) for experiments.</td>
</tr>
<tr>
<td><strong>rf quadrupole $q_2$ value</strong>&lt;br&gt;Eq 4.19 p. 4—27</td>
<td>$q_2 = \frac{2 \cdot q \cdot V_{pp}}{m \cdot r_0^2 \cdot \omega^2} = \frac{4 \cdot q \cdot V_{0p}}{m \cdot r_0^2 \cdot \omega^2}$&lt;br&gt;A stability parameter for rf quadrupoles: $q$ (un-subscripted) is the ion charge, $V_{pp}$ is the peak-to-peak and $V_{0p}$ is the zero-to-peak applied rf voltage, $m$ is the ion mass, $r_0$ is the quadrupole ‘inscribed’ radius, $\omega$ is the rf frequency in radians per second ($= 2\pi f$).</td>
</tr>
<tr>
<td><strong>effective potential energy for quadrupole ion guides</strong>&lt;br&gt;Eq 4.40 p. 4—33</td>
<td>$V^*(r) = \frac{q_2}{8} \cdot q \cdot V_{pp} \cdot \left(\frac{r}{r_0}\right)^2$&lt;br&gt;The theoretical average kinetic energy ‘stored’ in ‘wiggling’ motion during low $q_2$ (&lt; 0.4, see above for definition) ion motion in rf quadrupoles: $r$ is ion radial displacement, else as above.</td>
</tr>
<tr>
<td><strong>dominant period of ion motion for ‘low $q_2$’ trajectories</strong>&lt;br&gt;Eq 5.13 p. 5—48</td>
<td>$T_0(\omega) \equiv \frac{T_0}{T_\omega} \approx \frac{2\sqrt{2}}{q_2}$&lt;br&gt;Theoretical average period of rf cycles required for one complete period of the broader ion motion (on top of which happens the ‘small wiggling’ motion).</td>
</tr>
<tr>
<td><strong>rf cycle ‘length’ of an ion trajectory</strong>&lt;br&gt;Eq 4.28 p. 4—29</td>
<td>$L_{nf} = \frac{\omega \cdot l}{2\pi} \cdot \sqrt{\frac{m}{2 \cdot K_z}}$&lt;br&gt;The dimensionless ‘length’ of an rf quadrupole region defined in terms of the number of rf cycles that ions experience: $K_z$ is the ion kinetic energy in the z-direction, $l$ is the physical length of the quadrupole region, and $f = \omega/2\pi$ is the rf frequency. Assumes constant speed in the z-direction.</td>
</tr>
</tbody>
</table>
### Kinetic Energy Available for Conversion or Reaction

For two masses $m_1$ and $m_2$ with initial velocities $u_1$ and $u_2$ colliding, with $v_{rel}$ the relative velocity of the two particles, this represents the portion of the kinetic energy that is available for reactions or for other conversions (e.g., rotations, vibrations). This neglects long-range forces such as screened Coulomb (e.g., between anion and neutral) or dipole induced attractions (see sections 6.2 and 6.3).

\[ K_R = \frac{1}{2} \left( m_1 u_1^2 + m_2 u_2^2 \right) - \frac{1}{2} \frac{m_1 m_2}{m_1 + m_2} v_{rel}^2 \]

### Kinetic Energy Available for Conversion or Reaction

As above but assuming the initial velocity of $m_2$ can be neglected, $K_0$ is the initial kinetic energy of $m_1$.

\[ K_R = \frac{m_2}{m_1 + m_2} K_0 \]

### Threshold Estimate for an Interaction

\[ T_e = K_R - \Delta_b \]

$K_R$ is the kinetic energy available for conversion as defined above. $\Delta_b$ is an estimate of or known energy barrier, endothermicity or exothermicity of the possible interaction, and is defined so that it is negative when the interaction would be exothermic. $T_e$ then gives a first-order estimate as to whether or not the interaction is likely, with positive values indicating the interaction is favourable.
1 Introduction

Mass spectrometry (MS) is one of the most wide-spread analytical techniques today. A suitable yardstick may be the vast body of dedicated international and peer-reviewed literature such as International Journal of Mass Spectrometry, Mass Spectrometry Reviews, Journal of Mass Spectrometry and American Journal of Mass Spectrometry. The particular branch known as Accelerator Mass Spectrometry (AMS) typically uses $\geq 0.5$ MV tandem accelerators to measure trace isotope abundances on the order of $\leq 10^{-12}$ (trace / abundant isotope ratio). Development of MS and its associated technologies is ongoing and widespread. This PhD thesis belongs mainly to that line of research with description of a new instrument that was initially intended to expand the applications of AMS systems, currently called an Isobar Separator for Anions (ISA).

Fundamentally, MS may be thought of as the art of filtration. Filters are typically based on acceleration, physical processes (eg. electron stripping and collision induced dissociation) and reactive or other chemical processes (eg. electron transfer and interactions with photons).

Primitive MS systems, as used by the forefathers of MS, W. Wien and J.J. Thomson, relied heavily on chemical sample preparation and pure acceleration-based filters for mass separation. Discussion of gas-phase isobar suppression during MS measurements came in 1989 (chapter 3).

Tandem accelerators were introduced as molecular filters that produce atomic cations at high energy that may then be further filtered in high energy dE/dx and ionization based detectors, as described further in the next section. Although the acceleration-based filters of such systems normally have low resolving power, $R_{FWHM} < 10^3$, AMS systems are currently the most sensitive kind of MS (eg. for $^{10}$Be, $^{14}$C, $^{129}$I, $^{41}$Ca) because of the wide variety and number of filters used. Initially, sample preparation aside, chemical filtration takes place in the ion source, molecular suppression occurs during electron stripping in the terminal of the accelerator, and nuclear and / or chemical filtration takes place in the detector (reviewed in Litherland et al. 2010).

The goal of this PhD thesis work was to develop a new filter based on low energy ion-gas reactions to separate isobars in an ion beam before the accelerator. Chemical reaction rates vary according to elemental and molecular properties so may be very isobar specific. Because of the considerable sensitivity of AMS, rare reactions and reaction cross sections not accessible experimentally with other methods may be accessible for study with an ISA-AMS system.
1.1 Guide to the Thesis

Different readers will want to focus on different elements of the thesis and so this guide should be consulted before reading. At the commencement of my doctoral studies I was neither an expert in accelerator mass spectrometry (AMS) nor familiar with rf quadrupole technology. The Isobar Separator for Anions (ISA), as it is currently known, was designed by IONICS Mass Spectrometry Group, Inc. (Bolton, Ontario, Canada), based on proven rf quadrupole technology. My work began at IsoTrace Laboratory (Toronto, Ontario, Canada) helping design and assemble a test-bed for the ISA and incorporating it into the existing AMS system.

A certain amount of bridging between the group at IsoTrace (experts in AMS) and the group at IONICS (experts with rf quadrupoles) was needed in order to properly address the challenges involved with this project. This body of work represents a comprehensive analysis of both the technology used for the ISA and its applications, and is accordingly rather lengthy.

Chapter 2 is meant to provide the technical motivations for undertaking this project. It reviews the challenges involved with ultra-sensitive isotope abundance ratio measurements and surveys technical advances.

Chapter 3 reviews some of the historical development of rf quadrupole instruments and ion-gas reaction cells, highlighting many useful references and discussing early work on gas-phase reaction based isobar separation.

Chapters 4 and 5 focus on the theory of rf quadrupole operation and design.

Chapter 4 reviews important mathematical concepts and provides equations needed to understand rf quadrupole operation. Many of these equations are referred to throughout the body of the thesis. A thorough reading of the chapter may not be necessary for those already familiar with the concepts.

Chapter 5 presents a simple but as yet (to the best of my knowledge) un-used ion trajectory simulation procedure that has some advantages over the traditional ‘matrix method’. Both methods are compared briefly. For those not interested in rf quadrupole design and ion trajectory properties it may suffice to simply read the discussions in sections 5.3.7 and 5.4.3.3.

The chapter is divided into two main sections. The first examines general ion trajectory properties in ideal rf quadrupole fields in the absence of fringing fields and does not consider space charge. It discusses the effects of varying initial conditions such as radial kinetic energy, position and rf phase. The second section discusses the effects of apertures and varying field
properties between adjacent rf quadrupole segments, especially useful for understanding experimental results reported in chapter 8.

Chapter 6 reviews elementary concepts for understanding gas-phase reactions and is useful for understanding the discussions in chapters 9 – 12. The end of the chapter uses the concepts to examine work done at Oak Ridge Laboratory where a ‘cooling cell’ was used with a laser for isobar separation relevant to AMS. Particular attention was paid to this work because there are some similarities with the ISA.

Chapter 7 describes the experimental system and gives manufacturer information for the materials used during my doctoral studies. The last section describes a new technique for studying anion-gas reactions using the ISA with an AMS system. Results of experiments using the technique are reported in chapters 10 and 12.

Chapter 8 discusses vacuum transmission through the ISA and experimental results are shown to be consistent with the modelling work done in section 5.4.3.

Chapter 9 provides an elementary theoretical treatment of cooling based on a ‘hard sphere’ approximation. The second half reports ion transmissions through the ISA with 6 mTorr pressure CH₄, Ar and NO₂ (for highly non-reactive experiments). It is shown that results are consistent for a variety of anions, and are consistent with those from Oak Ridge.

Chapter 10 is again divided into two major sections. The work was initially carried out to assess the best reaction and/or cooling gases for ⁳⁶Cl applications, but also examined the origins of reaction loss plateaus noted during many measurements with NO₂. The first section examines Cl⁻ transmission through the ISA with various gases and discusses loss channels. The second looks at C₃⁻, S⁻ and SO⁻ transmissions through various gases. The technique referred to in chapter 7 is used to study reaction channels.

Chapter 11 reports the successful measurement of \(4 \times 10^{-13} \leq ³⁶Cl/Cl \leq 4 \times 10^{-11}\) reference standards using the ISA with NO₂ gas and the IsoTrace AMS system at 1.75 MV.

Chapter 12 examines possible extensions of the ISA to ⁹⁰Sr applications and presents reaction data for the relatively exotic anions YF₃⁻ and ZrF₃⁻ with NO₂.

Chapter 13 summarizes the body of the thesis and compares some results to work done by other groups using other methods.

I would like to thank all those who have been patient as I have struggled to find a balance between completeness, thoroughness and finiteness.
2 Background

This section provides a broad overview of MS and AMS, and a discussion on technical and instrumental demands for trace isotope abundance analysis at \( \leq 10^{-12} \) (= trace / abundant isotope measured ratio). The benefits of moving beyond purely acceleration-based filters for MS and employing every stage for isobar suppression are highlighted as motivation for the ISA project.

2.1 Mass

Mass itself is a very subtle quantity and it is relevant to discuss this briefly in a thesis on a new technology for “mass spectrometry.” It has long been known that there is a “vis insita,” some “innate force of matter” proportional to “mass” that manifests as a resistance to a change in some object’s motion, and “inertia” is the name adopted for this resistance (Newton 1687).

The idea that the effective mass of an object could be affected by motion, that inertia could change with velocity, appears to have first been proposed by J.J. Thomson in 1881. Experiments on the behaviour of electric discharges in gases under the influence of magnetic fields, particularly by Crooks and Goldstein, prompted Thomson to consider the effect of charge on the motion of charged particles. Although it had not yet been proven, he believed the discharges were composed of charged particles. Thomson (1881 p. 230) states, “Now, according to Maxwell’s theory, a variation in the electric displacement produces the same effect as an electric current; … and consequently the charged sphere must experience a resistance as it moves through the dielectric… In other words, it must be equivalent to an increase in the mass of the charged moving sphere, which we now proceed to calculate.” After calculation, Thomson (1881 p. 234) concluded that the effect of charge on the motion of a body (assumed spherical for simplicity) “…is the same as if the mass of the sphere were increased…”

This idea stimulated a surge of papers culminating in Einstein’s famous series of papers beginning in 1905 on the theory of relativity (reviewed by Hecht (2009). Einstein (1905) proposed the postulates of the Principle of Relative Reference Frames and that light is always propagated in empty space with a definite velocity regardless of the motion of any emitting body, deriving that mass and energy are proportionally related for electrons in motion. Generalized, if \( v \) is the speed of the particle measured relative to an observer, \( c \) is the constant speed of light in a
vacuum, $\beta \equiv \frac{v}{c}, \gamma \equiv \left(\frac{1-\beta^2}{1-\beta^2}\right)^{-\frac{1}{2}}, m_0$ is the particle’s mass as measured in its rest frame and $E$ is energy, Einstein’s famous equation of special relativity is:

**Eq 2.1**

$$E = \gamma m_0 c^2$$

Neglecting for the moment why $c$ should have such a fundamental significance, Eq 2.1 shows that as a massive particle moves faster relative to an observer there seems to be a build-up of resistance to it moving even faster. It is as if the inertia of a massive body increases with speed, imposing an upper bound to the attainable speed.

Equation 2.1 gives a relationship between energy and mass which is used in Appendix A.III. Equations in Appendix D (p. 259) describe how to calculate changes in atomic or molecular mass based on bonding energies, and this is also discussed briefly in Appendix C.I. The main point is that a compound is less massive than a simple sum of the masses of its constituent parts. This could be due to the parts themselves having structure or some of their mass being converted to energy or due to the presence of virtual particles or some other phenomena. As discussed in Appendix B.II, neutrons behave differently when combined than they do when isolated. In any case, what is called mass is anything but completely understood. It is not surprising that over 100 years after Einstein’s initial paper on relativity and 130 years after J.J. Thomson’s inquiry into the matter, a strong debate persists as to the appropriateness of referring to ‘relativistic mass’ (Adler 1987, Okun 1989, Letters 1990, Sandin 1991, Hecht 2009).

Attempts to answer fundamental questions about the nature of mass and gravitational interactions are still at the forefront of theory and experiment, for example the LHC at CERN (CERN 2010).

Relativistic effects are not needed to describe ion kinetics for the kinetic energies used in the experiments described in the body of this thesis. For example, a typical measurement for Cl work uses $\leq 6.8$ MeV $^{35}$Cl$^{+3}$ ions for detection. An ion with $m_0 = 35$ amu = 32595 MeV/c$^2$ that has been accelerated to 10 MeV has $\gamma m_0 = 32605$ MeV/c$^2$, $\gamma \approx 1.0003$ and $\beta \approx 0.025$. The “relativistic mass” is only 0.03% (see $\gamma$) greater than the ‘rest’ (intrinsic) mass, and the ion moves at 2.5% the speed of light ($\beta$), which does not require analysis with relativistic mechanics.

### 2.2 Mass Spectrometry and Filters

The mass of a body describes its resistance to changes in motion while applying a force to a body may cause acceleration. Bodies with different masses, then, will undergo accelerations
of different magnitude on application of a force of equal magnitude if the bodies interact with the force. Traditionally in MS, atoms and molecules are ionized so that static or time-varying electric and magnetic fields may be used to accelerate them. The charge may be thought of as promoting the acceleration while the mass opposes it so that these acceleration-based techniques separate ions according to $M/Q$ (mass-to-charge ratio).

The general MS process may be thought of as ionization $\rightarrow$ filtration $\rightarrow$ detection. There are numerous methods for each, and filtration may take place during ionization and detection. For example, use of atomic anions can greatly reduce the presence of inert gases and Mg and N in ion beams, and use of PbF$_2$ powder in a solid Cs$^+$ sputter target can promote specific fluorine molecular anion formation (Zhao et al. 2010a, b, c). Detectors with ion discrimination may be based on selective chemical reactions and, at high energy, differences in $dE/dx$, and if ion energy is above the Bragg peak, differential energy loss as ions pass through thin ‘windows’ (Krestow et al. 2007 p. 196, Eliades et al. 2010 fig. 4 and discussion). Ions may also be selectively dissociated in strong field gradients, as Nadeau et al. (1994) demonstrated for weakly-bound atomic anions. Several common acceleration-based MS filters are listed in Table 2.1.

The properties of a mass spectrometer depend on the ion source, detector(s) and other filters. Some important parameters are (many MS definitions may be found at IUPAC 2011):

- **Dynamic range**: for a detector it is defined in terms of the detection range as the ratio of the largest to smallest detectable signal
- **Ion beam intensity limit**: defined here as the maximum current that can be injected into a filter without unwanted losses from scattering, space charge effects or other phenomena
- **Transmission**: defined here as the ratio of a particular $M/Q$ signal before and after one, several or all of the mass spectrometer elements
- **Resolving power**: $R = M/\Delta M$ where $M$ is mass and $\Delta M$ is the width of a peak in a mass spectrum at some percentage of the maximum peak height such as the full width at half the peak maximum (FWHM). Resolving power and theoretical peak spectra are discussed at length in Appendix D (note that here $\Delta M \neq \Delta M_{XY}$, see first paragraph in Appendix D.I).
- **Mass accuracy**: $\frac{(M - M_{measured})}{M}$
- **Analysis time**: the time taken to measure a mass peak/spectrum. This is especially important for high sample throughput demands.
- **Vacuum quality**
Table 2.1: Common Acceleration-Based Filters in Mass Spectrometry

<table>
<thead>
<tr>
<th>Filter Type</th>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static Magnetic Analyzer</td>
<td>((B\rho)^2 = 2 \cdot \frac{m}{Q} \cdot \frac{K}{Q} = \left( \frac{p}{Q} \right)^2)</td>
<td>(B ) magnetic field strength, (\rho) radius of trajectory, (m) mass, (K) kinetic energy, (p) momentum, (Q) charge</td>
</tr>
<tr>
<td>Static Electric Analyzer</td>
<td>(E\rho = 2 \cdot \frac{K}{Q} = v^2 \cdot \frac{m}{Q})</td>
<td>(E) electric field strength, (v) speed, else as above</td>
</tr>
<tr>
<td>Wien (speed) filter</td>
<td>(\frac{E}{B} = v)</td>
<td>as above, crossed static electric and magnetic fields</td>
</tr>
<tr>
<td>Time of Flight (TOF)</td>
<td>(t = d \cdot \sqrt{\frac{m}{2K}} = d \cdot \sqrt{\frac{m}{2 \cdot Q \cdot V}})</td>
<td>(t) time, (d) distance, (V) applied acceleration voltage, else as above</td>
</tr>
<tr>
<td>Ion Cyclotron Resonance (ICR)</td>
<td>(\omega^{-1} = \frac{2\pi}{B} \cdot \frac{m}{Q})</td>
<td>(\omega = 2\pi f) where (f) is the ion orbital frequency, else as above</td>
</tr>
<tr>
<td>Orbitrap</td>
<td>(\omega^{-1} = \sqrt{\frac{m}{k \cdot Q}})</td>
<td>(k) is an instrumental constant describing field curvature, else as above</td>
</tr>
<tr>
<td>Multi-pole with time-varying electric fields</td>
<td>(a_n = 2n \cdot (n-1) \cdot \frac{Q}{m} \cdot \frac{U'<em>a}{\omega^2 \cdot r_0^2}) (q_n = n(n-1) \cdot \frac{Q}{m} \cdot \frac{V</em>{pp}}{\omega^2 r_0^2})</td>
<td>(n) order of pole ((n = 2) for quadrupole), (U'<em>a) applied static voltage between neighboring poles, (V</em>{pp}) peak-to-peak time-varying voltage between pole pairs with frequency (\omega/2\pi), (r_0) inscribed radius of poles; (a_2) and (q_2) are stability parameters for quadrupoles (see discussion at Eq 4.31/32 regarding (n &gt; 2))</td>
</tr>
</tbody>
</table>

Obviously the type, number and arrangement of filters will vary according to application, and there is usually a trade-off between resolution, instrument size, ion beam current and cost. Currently, mass spectrometers that use Fourier Transform (FT)-ICR, FT-Orbitrap and TOF as ion discriminating detectors have the largest resolving powers and are used widely in biological studies, recently reviewed in Liu et al. (2007), and the petroleum industry. In these applications there is particular emphasis on analysis time, resolving power and mass accuracy. Liu et al. (2007 p. 3623) discuss amino acid identification related to proteomics research. A mass accuracy of 1 part per million (ppm) can exclude 99% of peptides that have the same nominal mass but different elemental composition (Liu et al. 2007 p. 3623).

Longer residence time in the analyzer may produce better resolving power and relative mass accuracy, but decreases throughput and transmission. Trap based filters are also typically
limited in dynamic range ($\leq 10^4$) and ion beam intensity limit, although large cyclotrons have existed since the 1930’s and have been used for very large ion current applications (Parkins 2005). When the mass scan is limited to a very narrow or single M/Q, higher $R_{\text{FWHM}}$ is typically obtained.

FT-ICR mass spectrometers require powerful and highly stable magnets and high vacuum ($< 10^{-7}$ Torr), but have the largest resolving powers ($> 10^5$) and mass accuracy (sub ppm). In most systems, ion currents are limited because of space charge interferences during signal detection and large energy spreads must either be collapsed through cooling or by discarding ions outside a given energy range. The dynamic range is mostly limited to $< 3$ orders of magnitude and $R_{\text{FWHM}} \sim 10^5$. However, $R_{\text{FWHM}} = 2 \times 10^8$ has been demonstrated for measurement of electron ionized $^{40}$Ar and $^3$He in a beam of single M/Q (Marshall 2000) and $8 \times 10^6$ for ions of a narrow M/Q range from bovine ubiquitin (~ 8000 amu) ionized by electrospray ionization (ESI) using a 9.4 Tesla magnetic field with a reduced number of ions (Shi et al. 1998). More recently Han et al. (2008) used a 12 Tesla magnet to achieve $R_{\text{FWHM}} \sim 10^5$ in a dynamic range $\leq 750$ with mass accuracy $\leq 0.65$ ppm in a mass range 90–570 amu and a measurement time of a few minutes. Schaub et al. (2008) used a 14.5 Tesla magnet to achieve a $R_{\text{FWHM}} = 8 \times 10^5$ at M/Q = 400 by combining 500 individual measurements with 3s scan times. In both recent (2008) cases, ions were first trapped in an octopole ion trap prior to injection to the FT-ICR, Schaub et al. (2008) reporting a trap capacity of $10^7$ charges.

The recently developed Orbitrap also uses resonant orbital signals for M/Q identification but without the demands of powerful superconducting magnets, however with similar ion current restrictions (Marakov 2000, Hu et al. 2005). Combined with a linear ion trap mass spectrometer, a nominal $R_{\text{FWHM}} = 60000$ over a dynamic range of 5000 for M/Q = 400 was demonstrated for a 1s scan cycle. A nominal $R_{\text{FWHM}} > 100000$ was also demonstrated possible with a 1.9s scan cycle (Marakov et al. 2006).

There are a broad range of TOF systems. Most operate with a dynamic range $\leq 10^4$ and $R_{\text{FWHM}} \leq 10^4$. However, the ABSciex (2011) 5600 TripleTOF System reports $R_{\text{FWHM}} = 3 \times 10^4$ with a linear dynamic range of $10^4 – 10^5$ over $150 \leq \text{M/Q} \leq 650$ at 100 spectra/s and sub-ppm mass accuracy. Ugarov et al. (2009) have reported on an improved Agilent quadrupole TOF system that has $R_{\text{FWHM}} > 2 \times 10^4$ for M/Q > 200 with low-mass cut-off at 50 amu and mass accuracy $\sim 0.5$ ppm at 20 spectra/s, and generally $R_{\text{FWHM}} > 2.5 \times 10^4$ for lower masses while for higher mass $R_{\text{FWHM}} > 4 \times 10^4$. Piechaczek et al. (2008) reported a TOF system for isobar
separation for the study of radioactive ion beams (RIB) with \(5.9 \times 10^4 \leq R_{\text{FWHM}} \leq 1.1 \times 10^5\) corresponding to 0.665 – 9.707 ms/scan when analyzing N\(_2\).

Makarov (2009) has summarized some of the broad aspects of the above systems as used in biological and petroleum analyses, shown here in Table 2.2.

Table 2.2: Typical Performance of Mass Spectrometers used in Biological and Petroleum Analyses*

<table>
<thead>
<tr>
<th>Detector</th>
<th>Dynamic Range**</th>
<th>(R_{\text{FWHM}})</th>
<th>Mass Accuracy (ppm)</th>
<th>Optimum Signal Range (ions/s)</th>
<th>Transmission (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOF</td>
<td>(\leq 10^4)</td>
<td>(10^4)</td>
<td>1.5</td>
<td>7000 – 5000</td>
<td>4</td>
</tr>
<tr>
<td>FT-Orbitrap</td>
<td>(\leq 10^4)</td>
<td>(6 \times 10^4)</td>
<td>0.65</td>
<td>500 – 5 (\times 10^5)</td>
<td>40</td>
</tr>
<tr>
<td>FT-ICR</td>
<td>(\leq 10^4)</td>
<td>(10^5)</td>
<td>0.1</td>
<td>500 – 5 (\times 10^5)</td>
<td>10</td>
</tr>
</tbody>
</table>

* These are representative values for mass spectrometers widely used in biological and petroleum analyses based on three mass discriminating detection methods, from Makarov (2009). See discussion above for more details.

** not from Makarov (2009)

Separation of almost 90% of the isobars listed in Table D 1 requires > \(10^4\) resolving power, and more than 40% require \(10^5 – 10^6\) resolving power, as shown in Figure D 1 (Appendix D), if the abundances were equal. While there are examples of TOF, FT-Orbitrap and FT-ICR systems with such resolving power, the rare isotopes of interest in AMS are typically in the ratio of rare isotope / isobar relative abundance < \(10^{-5}\), beyond the dynamic range of such instruments. Furthermore, at \(10^{-5}\) abundance ratio, the required \(R_{\text{FWHM}}\) is almost 2 times as great as the \(R_{\text{FWHM}}\) required when the abundance ratio is equal, assuming the signal peak may be described by a Gaussian curve (Table E 1, Appendix E). This problem is compounded by the non-Gaussian, wider peak shape that may be expected at lower abundance ratios, discussed briefly in Appendix E. Peaks tend to spread for a variety of reasons, including scattering, ion beam energy spread and system optics. The onset of such a spread may be seen in the TOF peak in Figure 1 p. 4512 of Piechaczek et al. (2008), only 1 order of magnitude below the peak maximum.

In any case, the optimum signal range for these instruments tends to be very high in the context of rare isotopes and very low in the context of abundant isotopes of interest in AMS, as will be discussed in the next section. Such systems alone, in their current state, are still not suitable for rare isotope analysis (abundance ratios \(\leq 10^{-12}\)). However, addition of other types of
filters may make them useful in the future. For example, TOF, FT-ICR and FT-Orbitrap mass analyzers are necessarily pulsed, there is a required residence time for ions in the instrument before M/Q may be measured. Often they function as traps, with ions traversing the detection region multiple (often hundreds) of times. Many systems incorporate a multi-pole trap before the mass analyzer in order to both accumulate ions and also to perform gas cooling (see sections 3.1, 6.4 and 9.2) to reduce the ion packet energy spread. If an appropriate gas were chosen it could also act as a chemical filter to remove unwanted isobars. Ion beam filters based on reactions are the subject of this thesis, to be discussed in more detail in the following chapters.

Dipole magnets have several advantages despite the fact that they are typically limited to $R_{\text{FWHM}} < 10^3$. Magnets may be designed for use with a very broad range of ion currents, lower than single ions per day to greater than mA of current, and are useful over a very broad range of ion kinetic energy, from sub eV to greater than MeV. With proper optical and vacuum design they also have large transmission over a very broad range of M/Q, essential characteristics for rare isotope measurement.

2.3 Trace Isotope Abundance Measurements

Trace isotope measurements in the context of accelerator mass spectrometry (AMS) typically require abundance ratios between a rare isotope $Y$ to an abundant isotope $X$, or several isotopes $X_i$, of $Y/X$ or $Y/\Sigma X_i \leq 10^{-12}$. Usually $Y$ is a radioisotope and $X$ is a stable isotope of the same element, for example $^{14}C$ and $^{12/13}C$ or $^{36}Cl$ and $^{35/37}Cl$, although there are cases, such as $^{99}Tc$ for which there is no known stable isotope, where this is not possible (see Table D 1 of Appendix D). Applications for such rare isotopes have been reviewed elsewhere (Kutschera 1990, Brown et al. 2006, Hellborg and Skog 2008, Litherland et al. 2010) and include geochronology, nuclear physics and environmental and medical research. The first wide-spread application was $^{14}C$-dating of archaeological artefacts based on the counting of decay events (Libby et al. 1949, Arnold and Libby 1949). Appendix B discusses some basic issues surrounding radioactivity and outlines relevant fundamental equations.

The main disadvantages of direct decay counting are sample size, detector limits and analysis time demands in the case of long-lived ($\tau_{1/2} \geq 1000$ years) isotopes. On the other hand, if a suitable ionization process and adequate filters are available for direct atom counting analysis by MS then these problems may be greatly reduced, as highlighted in the example at the end of
Appendix B for $^{14}$C. A brief illustration of the main points will be made here using the example of $^{36}$Cl since it was used in the first application of the ISA.

Doupé (2004 p. 2a) lists representative ranges for $^{36}$Cl/Cl from various natural sources. Most values are in the range $10^{-15} \leq \frac{^{36}\text{Cl}}{\text{Cl}} \leq 10^{-13}$ with the lowest for seawater ($^{36}$Cl/Cl $\leq 10^{-15}$, p. 136). Assume that a ratio $^{36}$Cl/Cl = $10^{-14}$ and at least 1000 counts of $^{36}$Cl were desired (counting statistics $\frac{1}{\sqrt{1000}} = 3\%$). For equations and notation refer to Appendix B; $M_{^{36}\text{Cl}} \approx 36$, $N_A \approx 6.022 \times 10^{23}$, $\tau_{1/2} = 3.01 \times 10^5$ years.

- **Decay counting**: for a $^{36}$Cl count rate of $\Delta N/U/\Delta t = 1$ c/min, 1.365 kg Cl would be needed (equation B13), and it would take 17 hours to accumulate 1000 counts with 100% detection efficiency. The average Cl content of seawater is 35g/L, so that this corresponds to 39L of seawater. If a reasonable sample size were 100 g Cl ($\approx 3$L seawater), this analysis would take about 10 days (equation B13).

- **MS atom counting**: for a $^{36}$Cl count-rate of 1 c/min = 0.017 c/s, 0.267 $\mu$A Cl would be required (equation B14), corresponding to 6 $\mu$g Cl over 17 hours (equation B15). In AMS, Cs$^+$ sputter sources are capable of producing many $\mu$A anion currents. If the sputter source produced 16 $\mu$A Cl$^-$, 1000 counts of $^{36}$Cl$^-$ would be accumulated in about 17 minutes, and production of 1 $\mu$A Cl$^-$ would require 4.5 hours counting time. Even if there were only 10% ionization efficiency, reasonable for Cl$^-$ from Cs$^+$ sputter sources, and 1% transmission through the AMS system (very low value), 1000 times the Cl material would be needed, corresponding to only 6 mg Cl. For seawater at 35g Cl/L, this would correspond to $< 0.2$ mL water sample.

From this comparison it can be seen that direct atom counting has the potential to reduce decay counting sample size and analysis time demands by orders of magnitude. In the case of ancient artefacts or medical work, the amount of sample material may be limited, and shorter analysis times can increase the sample throughput of a laboratory. In the case of remote geological studies, smaller sample size requirements can greatly increase the scope of research.

On the other hand, atom counting is only possible when isobars can be sufficiently resolved. When dealing with very low abundance ratios, isobaric interferences represent a major obstacle for detection of long-lived ($\tau_{1/2} \geq 1000$ years) radioisotopes. Isobaric interferences may be suppressed with instruments of high resolving power, ionization processes that do not favour the isobar, and through appropriate ion beam interactions (for example with gases or photons).
As outlined in the last section, acceleration-based MS filters alone are still currently not adequate. Furthermore, assuming Gaussian peak shapes as in Appendix E, in order to resolve two peaks for isobars X and Y with masses $M_X$ and $M_Y$ and relative signal intensity $Y/X = I_{XY}$ (rare/abundant),

$$R \geq \frac{1}{2\sqrt{\ln(h^2)}} \cdot \frac{M_X}{\Delta M_{XY}} \cdot \left( \sqrt{\ln(u \cdot I_{XY})^{-1}} + \sqrt{\ln(u^{-1})} \right) \quad (E\ 9).$$

Here, $R$ is the required resolving power at a fraction $h$ (e.g. at FWHM, $h = 0.5$) of the maximum peak height such that the rare isotope peak will be $u$ times the tail of the peak from X. Equation E 9 describes the broadening of the curve away from the peak. The resolving power required for $Y/X = I_{XY} = 10^{-6}$ is twice that required when $I_{XY} = 1$ (Table E 1). In fact, peaks shapes tend to be broader than a Gaussian distribution at small fractions of the peak maximum so that this is only an approximation.

The ideal case for MS would be a selective ion generation method (ionizes the isotopes of interest and not their isobars) that took place in a volume that could also quantifiably measure the isotope abundance ratios. This may be decomposed as follows,

- **Ion generation should be:**
  - stable, producing an ion count rate that is stable and sufficiently large of the rare isotope being studies for analysis in a short time (see Appendix B, equation B14)
  - selective, based on an ionization process such that isobars are either not ionized, or are ionized preferentially with different M/Q than the isotope of interest.
  - efficient enough to analyze small samples (see Appendix B, equation B15)
  - clean, not introducing new contaminants to the system as may happen with Secondary Ion Mass Spectrometry (SIMS) ion sources (Eliades 2006)
  - clean again, having a negligible ‘memory’ meaning that contamination from other samples previously analyzed should not be introduced in the ion source.

- **Filters should be able to resolve isobaric interferences sufficiently well for discrimination at levels of interest.** Such filters may include acceleration, reaction and physically based principles, or other, either separately or in combination.

- **Detectors must have sufficient dynamic range to quantifiably measure the signal from the isotope of interest.** Ideally, such a detector would also be able to resolve isobars.
2.4 Mass Spectrometry with Tandem Electrostatic Accelerators

Considerations of the last two sections led to the use of tandem accelerators as filters for trace isotope analysis. As Lord Illingworth states in the play *A Woman of no Importance*, “Moderation is a fatal thing, Lady Hunstanton. Nothing succeeds like excess.” (Wilde 2000, p.150). The history of development and basic principles have been covered elsewhere (Kilius 1980, Litherland 1980, Elmore and Phillips 1987, Litherland *et al.* 1987, Hellborg and Skog 2008, Litherland *et al.* 2010). A short review follows, see Figure 2-1 for an illustration of the principles outlined in this section.

Most AMS systems use a Cs⁺ sputter ion source and so are a form of Secondary Ion Mass Spectrometry (SIMS). Such sources were found to enhance anion production and produce large anion currents, easily exceeding μA in many cases (extensively reviewed in Middleton 1990). The ion beam is accelerated to > 20 keV to compensate for space charge expansion and initial energy and angular spread, and analyzed by static electric and magnetic analyzers (see Table 2.1). In most systems, the magnetic analyzer may be ‘bounced’ by applying a variable high voltage to accelerate ions to higher energy so that rapid scanning of ME/Q² is possible without changing the magnetic field (see Table 2.1).

The anions are then typically injected into a tandem accelerator where they are accelerated, generally to V ≥ 0.5 MeV. A ‘stripping device’ is located at the high voltage terminal, usually consisting of a foil or a gas cylinder. In this region electrons are stripped from the anions and subsequent neutrals and cations. With appropriate energy and collision dynamics a high yield of a particular cation may be produced. These are then repelled from the + high voltage terminal, so gain a further acceleration of QV, where Q is the + charge state after stripping. Basically, the tandem accelerator is used for molecular fragmentation at high energy and provides high energy fragments for detection with high energy detectors. At high energy, scattering angles are reduced, reducing angular spreads so that a high transmission is possible. On the other hand, at lower terminal voltages multiple collisions may be necessary for molecular interference suppression, requiring a “thicker” stripper (eg. higher gas pressure), which may lead to larger losses from scattering. If lower terminal voltages were desired then use of a less massive collision target, such as He, could partly compensate for the increase in number of collisions.
Another series of static electric and magnetic analyzers is then used to separate the resulting M/Q and E/Q. For low count rates ($\leq 10^4$ ions / second at IsoTrace) of the high kinetic energy cations, $dE/dx$ or ionization detectors may be used for simultaneous discrimination and counting while larger cation beams may be measured in Faraday cups. Some systems use a suitably thin foil or canal with a gas at a suitable pressure after the accelerator for further stripping at higher energy, and some have also employed TOF for detection.

As illustrated in Figure 2-1, some of the advantages of such AMS systems include (compare with second bulleted list from last section, p. 2—12):

- Cs$^+$ sputter ion sources:
  - May be used to produce large and stable anion currents
  - Use of atomic anions has proven very effective for isobar suppression in some cases, such as $^{14}$N suppression for $^{14}$C ($^{14}$N$^-$ is not stable) and $^{129}$Xe suppression for $^{129}$I
(although Haberland et al. (1989) observed very weak signals of Xe\(^-\) using TOF and electron attachment processes in Xe + Ar + N\(_2\))

Recent work has shown these ion sources are also effective for isobar suppression in some cases through enhanced element specific production of fluorine molecular anions (Zhao et al. 2010a, b, c)

- The electric and magnetic analyzers can be used for large ion currents
- With appropriate terminal voltage and stripper conditions, molecular anions can be dissociated into fragments with high yield for a particular charge state. There are several ways that this can be used to advantage, including:
  - Atomic and molecular anion isobar separation, eg. \(^{12}\text{CH}_2^-\) and \(^{13}\text{CH}^-\) dissociation for \(^{14}\text{C}\) detection and measurement
  - Molecular isobar suppression, eg. select conditions for preferential dissociation of one molecular isobar over the other, or use the molecular cation fragment spectrum after the accelerator to identify the molecule of interest (example given in section 10.3.2)
- With appropriate conditions, complete electron stripping can be used; employing additional strippers after the terminal may also be used for even higher energy stripping yields. A recent example using full nuclear stripping for \(^{36}\text{Cl}\) and \(^{36}\text{S}\) isobar separation may be found in G.-Uribarri et al. (2009)
- The electric and magnetic analyzers after the accelerator may again be used for large current and high energy ion beams
- High energy detectors may be used, for example based on dE/dx for identification of nuclear properties or ionization detectors for charge state identification

The early need for detectors capable of isobar resolution is discussed in Lee (1988). Particularly, charge-changing, electron detachment and molecular dissociations that allow unwanted ions to enter the final detector despite the ME/Q\(^2\) and E/Q filters is illustrated and discussed for \(^{14}\text{C}\) analysis (eg. Figures 33 and 36 p. 97, 101).

### 2.5 Some Recent and Related Technical Advances for Lower Kinetic Energy Analyses

Over the last 20 years a great deal of research has gone into very small, sub-MV AMS systems that rely on the traditional AMS principles for rare isotope analysis using the +1 charge
state after stripping. Initially Lee et al. (1984) and Lee (1988) demonstrated the effectiveness of using the +3 charge state and higher terminal voltages (2 MV) for molecular isobar suppression during $^{14}$C analysis, and had attempted using lower charge states (+1, +2) with limited success. A decade later, Suter et al. (1997) and Suter (1998) reported initial research into the feasibility of smaller and cheaper AMS systems operating below 1 MV, Hughey et al. (1997) reported on the design of a 1 MV AMS system, and Mous et al. (1997) reported on the construction of a compact (2.25 m x 1.25 m) 1 MV AMS system for biomedical research. The majority of these systems use higher pressure gas strippers in the accelerator terminal with larger apertures and more pumping than traditional systems.

By 2000, small AMS radiocarbon facilities operating at terminal voltages below 1 MV had opened (Suter et al. 2000). More recently, a “tabletop” 2.5 m x 3 m, 200 kV compact radiocarbon system (Synal et al. 2007) and a compact dedicated biomedical $^{14}$C analysis system (Synal et al. 2008) have been produced. Currently, compact “tabletop” 1 MV AMS systems are available from High Voltage Engineering Europa (HVEE) and 250 kV from National Electrostatics Corp. (NEC). Jull and Burr (2006) discuss some of the developments in smaller AMS systems surrounding ion sources and detectors, and point out some novel and interesting applications.

Compact systems are proving effective for routine radiocarbon analysis, and some novel research into new AMS measurement techniques has been possible with them (Wilcken et al. 2008). However, application of sub-MV AMS systems is currently relatively limited for isotopes other than radiocarbon, although a recent report suggests that it is possible to achieve > MV AMS background levels for $^{10}$Be measurements on a 0.6 MV system (Müller et al. 2008). On the other hand, 1 MV systems seem to be capable of performance similar to higher energy accelerators for most of the isotopes commonly measured by AMS (Chamizo et al. 2008). Higher energy AMS systems are still required for more sensitive samples, and smaller systems still cannot handle all isotopes of interest (notably $^{36}$Cl and $^{41}$Ca).

Approaches using lasers for either isotope detection or isobar suppression have received less attention. In 1994 Murnick and Peer described a new technique of detecting stable carbon isotopes in the gas phase using “laser optogalvanic effect spectroscopy”. A sample of CO$_2$ gas is maintained at a low power discharge and irradiated with light from a CO$_2$ laser, causing resonant molecular transitions that change the population of excited molecular states, causing a change in the electron energy distribution function. There is a corresponding change in the effective
impedance of the gas discharge which can be used to identify isotopes and quantify their relative proportions. Currently the lowest $^{14}\text{C}/^{12}\text{C}$ ratios that have been reported by Murnick et al. (2008) are on the order of $10^{-12}$, and they estimate the lower limit of their background to be $10^{-15}$.

Advantages of the technique are that it uses laser-induced resonance effects so it can be highly selective, effectively side-stepping the isobaric interferences important in AMS, and by its nature is useful for direct measurement of samples in the gas phase. The system is also relatively compact, can analyze small sample sizes on the order of 10 $\mu$g, and analysis does not consume the sample (which may be fed to another instrument down-stream for further analysis). However, an obvious draw-back is the specificity of the device. With the current technique, both $^{13}\text{CO}_2$ enriched $^{12}\text{CO}_2$ and $^{14}\text{CO}_2$ lasers are required for radiocarbon measurements, as well as an intimate knowledge of the resulting spectra. Application to other isotopes of interest in AMS, requiring sensitivity on the order of $10^{-14}$ or less, is necessarily quite complicated.

Berkovits et al. (1989) tested the feasibility of photon induced electron detachment for removal of $^{36}\text{S}^-$ in $^{36}\text{Cl}^-$ ion beams during AMS analysis. A beam of $\lambda = 532$ nm (2.33 eV) photons was produced from a frequency doubled Nd:YAG laser in 10 ns pulses with density $> 10^{17}$ photons/cm$^2$. Ion beams were accelerated to 100 keV and the ion-photon interaction region was 1.2 m. No significant $^{37}\text{Cl}^-$ losses were observed while a $^{32}\text{S}^-$ attenuation $\sim$ 3 orders of magnitude was measured with a photon–ion interaction cross section of $1.0 \pm 0.2 \times 10^{-17}$ cm$^2$.

The group at Oak Ridge National Laboratory, U.S.A., has recently reported work on non-resonant laser induced electron photodetachment to neutralize the unwanted isobar while leaving the isotope of interest unaffected. A He gas radio-frequency quadrupole cooling cell has been used to slow ions from keV kinetic energies to on the order of tens of eV kinetic energies for ion ‘cooling’. Cooling reduces ion kinetic energy, confining ions to a more narrow region around the axis and increasing the residence time within the ion–photon interaction region (the cooling cell), facilitating more ion–photon interactions. Suppressions of $\text{S}^-/\text{Cl}^-$ by $3 \times 10^{-4}$ and $\text{Co}^-/\text{Ni}^-$ by one order of magnitude were achieved using a continuous wave Nd:YAG laser producing $\lambda = 1064$ nm (1.165 eV) photons (Galindo-Ulibarri et al. 2008, Liu et al. 2005). The system and results are discussed further in section 6.3.1.

On the other hand, Alton and Zhang (2008) have theoretically investigated using a 100 cm long superconducting solenoid for control of 5-20 keV energy ion beams. In this case, the solenoid field is used to confine the ions to a small region around the axis and highly efficient mirrors are used to amplify laser light intensity in order to increase beam interaction. Theoretical
calculations for three isobar systems indicate this technique could achieve relative suppressions below $10^{18}$ for Co from Ni, and $10^6$ for S from Cl, roughly what would be needed to allow small AMS systems to handle isotopes such as $^{36}\text{Cl}$. The major advantage to this system is that it seems to be capable of handling the large energy spreads (discussed in section 10.3.6) from Cs$^+$ sputter sources typical in AMS, while not resulting in beam loss. However, present purchase and maintenance costs would be prohibitive, and a relatively small rise in the He temperature (used to cool the magnet) can lead to a very dramatic system failure.

A final note is made here on a report by Knie et al. (1997) who used a ‘gas-filled’ magnet and detector with 5 $\Delta E$ measurement stages with trajectory position and angle analysis capabilities to effectively increase the resolution of the $^{36}\text{S}$ and $^{36}\text{Cl}$ isobar signal peaks in the final detector. While it was not a ‘low kinetic energy’ AMS development as an accelerator terminal voltage of 13.5 MV was used for stripping to $q = +9$, the $^{36}\text{S}$ blank was reduced by a factor of 300. This is discussed further in chapter 13.
3 RF Quadrupole Collision Cells – A Historical Context for the ISA

Devices based on alternating radial gradient quadrupole fields were initially developed as ion beam optical lenses for strong focussing in high energy accelerator applications. The idea to use time varying quadrupole fields for ion traps, guides and M/Q filters grew from this research early on, and the idea was first published by Paul and Steinwedel (1953). Soon after, the first radio frequency (rf)-quadrupole based ion guide and filter was patented (Paul and Steinwedel 1956; 1960) and other instruments based on similar principles were developed.

Mono- and multi-pole M/Q filters had several advantages over those based on static magnetic fields, including compactness, resolving power and M/Q scanning speed, although there are also disadvantages as outlined in section 2.2. A review of early development may be found in Dawson (1976 p. 1 – 6) and Gerlich (2004 p. 585), while Koppenaal et al. (2004) present a more recent historical review.

By the 1970’s “tandem rf-quadrupole mass spectrometers” were being used to study ion-gas and ion-photon interactions. Such instruments incorporate three rf-quadrupole sections: the first is for M/Q selection, the second is operated as an ion guide to facilitate interactions (eg. with gases or photons) or simply act as a drift region (eg. for analysis of meta-stables), and the third is another M/Q filter to separate the products. This “triple-quad” technique is also known as MS/MS. Yost and Enke (1978) proposed using such instruments to study molecular structure through molecular ion dissociation induced by collisions with gas atoms and molecules, known as collision induced dissociation (CID), presenting initial work with 10 eV kinetic energy ions. Previously such studies had been carried out using sector magnet based instruments, but rf-quadrupoles had the advantage of higher resolving powers, faster scan times and the ability to trap and guide ions at much lower kinetic energy (several and sub-eV instead of > keV). Douglas (1982) presents a brief review of MS/MS and a contemporary summary of CID theory.
3.1 RF-Multipole Collision Cells as Chemical Isobar Filters and Ion Coolers

A distinction in nomenclature appears in the literature for cooling-, collision- (for CID) and reaction- multi-pole cells. Since all three applications are based on interactions with associated cross sections, all three will be referred to generally as collision cells when specificity is not needed.

The first attempts to use MS/MS for isobar suppression came in the late 1980’s. King et al. (1988) attempted to apply low energy CID to break up molecular interferences present in glow discharge MS (GD-MS). The work was expanded by King and Harrison (1989) using Ar gas for CID at various pressures (< 5 mtorr), exploring different collision kinetic energies (4.4 eV – 95 eV lab frame) with various cation molecules. While results were promising, they noted limitations due to transmission losses that they attributed mainly to scattering when gas was used.

That year Douglas (1989) presented results from attempts at isobar suppression for Inductively Coupled Plasma MS (ICP-MS) using low energy CID with Ar gas. He noted similar total loss cross sections for both atomic and molecular ions, suggesting that both scattering and charge transfer with Ar were responsible for atomic ion losses. He states (p. 48), “This suggests that large gains in metal ion to molecular ion ratios will not be possible by ICP-MS-MS using the middle quadrupole as a collision cell for dissociation. This led us to try ion molecule chemistry in the middle quadrupole.” After presenting data for Ce+, CeO+ and Tb+ incident on air, he suggested (p. 48), “This result is preliminary but suggests that at least for some special cases (e.g. rare earth analysis), ICP-MS-MS combined with ion molecule chemistry my provide a way around persistent interferences… The performance gains discussed here involve little more than further optimisation of the existing technology…” He also suggested that ICP-MS-MS could be used for studying gas phase ion chemistry for most of the elements.

Rowan and Houk (1989) proceeded to use a two-quadrupole system directly coupled with an ICP source to demonstrate very selective and efficient ion-gas reactions for isobar suppression. Citing the two 1989 papers on isobar suppression with CID listed above, they reported attenuation factors of 50 – 400 for Ar2+, ArO+ and ArN+ while retaining 50 – 70% of the analyte ions, with best results for low energy collisions with Xe and CH4.

Use of buffer gases in multi-pole ion traps for energy transfer from incident ions (ion cooling) in order to damp oscillations and focus trajectories had been in practice for over 2
decades by 1990. However, the first observation of collisional cooling in an rf-quadrupole not operated as a trap was not made until 1992 (Douglas and French 1992). The aim of the research had been to determine the scattering loss cross sections of ions traversing a gas filled collision cell. Somewhat ironically, instead of seeing an expected increased loss with rising pressure, increased transmission was observed for pressures ranging from 2 – 8 mtorr.

All of this suggested that with appropriate initial ion energy and energy spread, gas pressure, collision cell design, and choice of collision gas, collision cells could be used for both isobar suppression and to increase transmission of analyte ions. This is fundamentally the basis of the ISA, the subject of this thesis. Subsequently, multi-pole cells for ion cooling and isobar suppression through reactions and CID were developed (eg. Barinaga and Koppenaal 1994, Tanner and Baranov 1999). The history of development and application has been reviewed extensively (eg. Paul 1990, Bandura et al. 2001, Tanner et al. 2002, Koppenaal et al. 2004).

Closely related to the present work are recent studies on anion cooling and isobar separation reported by Liu et al. (2002, 2007, 2009). The fundamental procedures are the same as the ISA: anions are produced in a Cs+ sputter source, accelerated to several keV and m/q analyzed, then decelerated, injected into the collision cell and then re-accelerated for analysis downstream. Instead of using chemical reactions for isobar separation as in the ISA, cooling with He is used to increase ion density near the central axis where laser light induces electron photodetachment from unwanted isobars. More discussion can be found in section 6.3.

### 3.2 General and Technical References

Multi-pole ion traps and mass filters, especially quadrupole instruments, are extremely popular in many fields of research and have attracted much attention since their inception. Accordingly there exists a veritable litany of theoretical and experimental publications involving multi-pole instruments. The broad review by Tanner et al. (2002) is a very comprehensive introduction to the subject with emphasis on experimental chemistry and reaction dynamics in multi-poles. The review by Douglas et al. (2005) has a technical focus with a broad theoretical overview. A much more concise physical introduction to the subject with a general discussion on popular applications is given in Paul (1990).

A very detailed theoretical and experimental treatise on quadrupole and monopole instruments can be found in Dawson (1976), while a more concise theoretical analysis is found in Pichanick (1967). March (1997) provides a theoretical and experimental introduction to ion traps, while March and Todd (2005) is a much more detailed text.
Gerlich (1992) provides a rigorous analysis of ion behaviour in quadrupole and higher order multi-pole fields in the context of the effective potential approximation, and discusses instruments composed of wire- and ring-electrodes. More recently, Gerlich (2004) reviewed the theory of multi-pole instruments including wire- and ring-electrode assemblies, while Baranov et al. (2005) discuss limitations of the effective potential approximation.
4 Ion Motion in RF Quadrupole Fields

A multi-pole field generated by a periodic potential of the form $\Phi(x,y,t)$ can generally be separated in Cartesian coordinates:

Eq 4.1

$$\Phi(x,y,t) = \phi(t) \cdot \sum_{n=0}^{\infty} A_n \cdot \phi_n(x,y)$$

where $n$ represents the order of symmetry and $A_n$ represents the amplitude of the $n$th-order spatial field contribution (harmonic), $\phi(x,y)$, to $\Phi(x,y,t)$. Typical rf multi-pole instruments are composed of $2n$ parallel cylindrical or hyperbolic conducting rods with applied sinusoidal rf and static (‘dc’) voltages. Figure 4-1 is a sketch of a typical rf-quadrupole ($n=2$) instrument, as used for the ISA, and defines some important parameters to be used throughout the remainder of this thesis. Oscillating quadrupole fields are also responsible for ion confinement in instruments known as monopoles that typically use one rf electrode rod (extensively reviewed in Dawson 1976 and Pichanick 1967). Quadrupole ($n=2$), hexapole ($n=3$) and octopole ($n=4$) instruments are currently the most common pole orders used for multi-pole instruments:

Eq 4.2 quadrupole

$$\phi_2 = \frac{x^2 - y^2}{r_0^2}$$

Eq 4.3 hexapole

$$\phi_3 = \frac{x^3 - 3xy^2}{r_0^3}$$

Eq 4.4 octopole

$$\phi_4 = \frac{x^4 - 6x^2y^2 + y^4}{r_0^4}$$

where $r_0$ is defined in Figure 4-1. A more extensive analysis is given in many of the references from section 3.2, particularly Douglas et al. (2005) and Gerlich (1992). Ion trap equivalents are discussed in Sudakov (2001) and March (1997), while Du et al. (1999) discuss field harmonics.

Ion oscillatory motion within rf multi-pole instruments is complex and may be described by a superposition of multiple periodic motions. In ideal and periodically oscillating quadrupole fields, ion trajectories have the special property that they can be reduced to a set of decoupled one-dimensional differential equations.

Distortions in an ideal quadrupole field, such as those arising from differences in rod diameters and spacing about the central axis or capacitive coupling between components, lead to higher order field terms such as hexapole or octopole where ion motion is no longer spatially
decoupled. A y-rod position offset by as little as 0.001r₀ for a round-rod quadrupole mass filter can lead to significantly reduced transmission, mass peak shifts and the appearance of major peak and tail structures in mass spectra (Taylor and Gibson 2008). This represents micro-metre machining precision demands when r₀ < 10 mm, which is the case for most systems. On the other hand, the usefulness of higher order harmonics for quadrupole mass spectrometry has been studied, and use of non-uniformly sized and positioned rods in a round-rod quadrupole instrument to produce specific field harmonic “islands of stability” has improved resolution, peak shapes and transmission in some cases (Du et al. 1999, Ding et al. 2003, Zhao et al. 2009).

Figure 4-1: Sketch of a General Cylindrical rf Quadrupole Instrument

RF-quadrupole instruments may be made from four parallel cylindrical rods arranged symmetrically about a central axis (z-axis). The minimum distance between rods and the central axis is labelled r₀, known as the “inscribed radius”. Diametrically opposite rods are given the same time-dependent potential V₀p(t) while neighbouring rods have the same magnitude of potential with opposite sign. Here V₀p(t) is the ‘0-to-peak’ amplitude of the rf voltage (1/2 the peak-to-peak rf voltage amplitude, see discussion after Eq 4.21) with constant frequency ω=2πf, and Uₐ is an applied static voltage. A further constant potential U can be applied to all four rods potentially creating an overall potential offset from other sections of the instrument and introducing fringing fields.
4.1 Basic Equations of Ion Motion in an Ideal Field

Paul (1990 p. 532) describes ions trapped in rf quadrupole cells as being “elastically” bound to regions by attractive forces that increase linearly with radial distance:

\[ F = m \frac{\partial^2 \vec{u}}{\partial t^2} = -k \cdot \vec{u} \]

where \( k \) is the binding constant, \( \vec{u} \) is a position variable and \( m \) is the mass of the ion. Relativistic effects have not been taken into account since most quadrupole systems like the ISA use relatively weak electric fields to accelerate ions to relatively low velocities (see section 2.1).

Assume that the force on the ions arises from an electric field present due to the application of an electric potential that can be separated into space (Eq 4.5) and time factors:

\[ \vec{F} = -q \cdot \nabla \cdot \Phi(x, y, z, t) = -q \cdot \nabla \cdot (\lambda(t)x\hat{x} + \kappa(t)y\hat{y} + \eta(t)z\hat{z}) \]

\[ \Rightarrow \Phi(x, y, z) = \frac{1}{2} (\lambda(t) \cdot x^2 + \kappa(t) \cdot y^2 + \eta(t) \cdot z^2) + U \]

where \( q \) is the charge of the ion, \( \nabla = \frac{\partial}{\partial x} \cdot \hat{x} + \frac{\partial}{\partial y} \cdot \hat{y} + \frac{\partial}{\partial z} \cdot \hat{z} \) is the gradient operator, \( \hat{u} \) is a unit vector in the direction of \( \vec{u} \), \( U \) is an arbitrary constant potential and \( \lambda, \kappa \) and \( \eta \) are coefficients that may be time-dependent. If charge density is \( \rho \) and the permittivity of free space is \( \varepsilon_0 \) then Poisson’s relation may be written:

\[ \nabla^2 \Phi = -\frac{\rho}{\varepsilon_0} \]

where \( \nabla^2 = \nabla \cdot \nabla \) is the Laplacian operator. If effects such as space charge are neglected then \( \lambda + \kappa + \eta = 0 \). There are an infinite number of solutions, but the most commonly used are:

\[ \lambda(t) = -\kappa(t) = \Phi_0(t); \eta = 0 \]

\[ 2\lambda = 2\kappa = -\eta \]

Since the ISA is operated as a collision cell ion guide, only Eq. 4.9 is discussed. From Eq 4.7:

\[ \Rightarrow \Phi(x, y, z, t) = \Phi(x, y, t) = \frac{\Phi_0(t)}{2} (x^2 - y^2) + U \]

Equation 4.11 resembles Eq 4.1 and shows that the quadrupole potential of Eq 4.2 with a possibly time-dependent amplitude can create the “elastic binding force” of Eq 4.5. Ideally, hyperbolic electrodes shaped according to Eq 4.2 for a constant value defining an equipotential
surface would be used. In practice however, 4 symmetrically spaced round rods of equal radius, as in Figure 4-1, are often used and the potential is not purely quadrupole.

The ratio of the round rod radius, \( r_r \), to the inscribed radius, \( r_0 \) (Figure 4-1), is important in both determining the field shape and the intensity of higher order harmonics. Douglas and Konenkov (2002) found that \( r_r/r_0 = 1.13 \) does not optimize the quadrupole field shape but does minimize some higher order harmonics and optimizes mass analysis with linear quadrupole mass filters. Taylor and Gibson (2008) found empirically and theoretically that \( r_r/r_0 = 1.127 \) is the optimum value for quadrupole mass filters. Rama Rao and Bhutani (2000) quote \( r_r/r_0 = 0.5375 \) for hexapoles and \( r_r/r_0 = 0.355 \) for octopoles made of round rods. More extensive reviews can be found in Tanner et al. (2002 p. 1391 – 1392) and Douglas et al. (2005 p. 3). The ratio for the ISA collision cell used for most of the experiments in this thesis was \( 1.159 \pm 0.002 \) (see section 7.4).

If a sufficiently large static potential difference were applied to 4 electrodes according to Eq 4.11, ions would be confined in one coordinate direction and dispersed in the other. If the potential were periodic with appropriately matched strength and frequency then the focussing would compensate for the dispersing before ions were lost. Although other potentials may be used (Richards et al. 1973), the most common form is \( V_{0p} \cos(\omega \cdot t + \theta) - U_a \). Substituting into Eq 4.11 at one of the electrode surfaces in a structure like Figure 4-1 (eg. \( \Phi_0(t) = \frac{\Phi_0(t)}{2} \cdot r_r^2 + U \)),

Eq 4.12
\[ \Phi_0(t) = \frac{2}{r_0^2} \left[ V_{0p} \cos(\omega \cdot t + \theta) - U_a \right] \]

where \( V_{0p} \) is the 0-to-peak amplitude of the time-varying potential with frequency \( f = \omega/2\pi \), \( \theta \) is the initial phase and \( U_a \) is an additional time-independent potential.

From Eq 4.11, the total applied potential is given by:

Eq 4.13
\[ \Phi(x, y, z, t) = \frac{1}{r_0^2} \left[ V_{0p} \cos(\omega \cdot t + \theta) - U_a \right] \cdot (x^2 - y^2) + U \]

Substitution into 4.6 using \( F_a = m \frac{\partial^2 u}{\partial t^2} \) yields three equations of motion:

Eq 4.14
\[ \frac{\partial^2 x}{\partial t^2} + \frac{2q}{m \cdot r_0^2} \left[ V_{0p} \cos(\omega \cdot t + \theta) - U_a \right] \cdot x = 0 \]

Eq 4.15
\[ \frac{\partial^2 y}{\partial t^2} + \frac{2q}{m \cdot r_0^2} \left[ U_a - V_{0p} \cos(\omega \cdot t + \theta) \right] \cdot y = 0 \]

Eq 4.16
\[ \frac{\partial^2 z}{\partial t^2} = 0 \]
Application of the idealized potential in Eq 4.13 to a 4-electrode arrangement like that of Figure 4-1 has led to three decoupled equations of motion, one of which has no acceleration from the resulting electric field. The periodic potentials are \( \pi \) out of phase between the x-rods and y-rods, and the static potential \( U_a \) has opposite sign in x and y.

In the x and y directions (x and y represented by \( u \)) the equations of motion have the form:

**Eq 4.17**

\[
\frac{\partial^2 u}{\partial t^2} + G(t) \cdot u = 0
\]

where \( G(t) \) is a single-valued periodic function of period \( 2\pi/\omega \) and may be represented by a Fourier series. The general Eq 4.17 is known as Hill’s differential equation, but when the Fourier series reduces to:

**Eq 4.18**

\[
G(t) = A_0 + A_1 \cos(\omega t)
\]

then Eq 4.17 is known as Mathieu’s differential equation, which has well-known properties.

Equations 4.14/4.15 have the same form as Eq 4.18. Re-parameterizing Eq 4.14/15 to reveal \( A_0 (= a_2) \) and \( A_1 (= 2q_2) \) results in the definition of ‘stability parameters’:

**Eq 4.19**

\[
q_2 = \frac{2 \cdot q \cdot V_{pp}}{m \cdot r_0^2 \cdot \omega^2} = \frac{4 \cdot q \cdot V_{0p}}{m \cdot r_0^2 \cdot \omega^2}
\]

**Eq 4.20**

\[
a_2 = \frac{4 \cdot q \cdot U'_a}{m \cdot r_0^2 \cdot \omega^2} = \frac{8 \cdot q \cdot U_a}{m \cdot r_0^2 \cdot \omega^2}
\]

**Eq 4.21** Units: \[
\left[ \frac{2 \cdot C \cdot V_{pp}}{kg \cdot m^2 \cdot (2\pi \cdot Hz)^2} \right] = 4.8880044 \frac{\text{charge} \cdot V_{pp}}{amu \cdot mm^2 \cdot MHz^2}
\]

The subscript on \( q_2 \) and \( a_2 \) represents the order of the pole symmetry, \( n \), as discussed for Eq 4.2 – 4.4, and these are the well-known dimensionless quadrupole stability parameters. The ion charge \([C]\) and mass \([kg]\) are represented by the un-subscripted \( q \) and \( m \) respectively. The periodic potential oscillates at the frequency \([Hz]\) \( f = \omega/2\pi \), and \( r_0 \) \([m]\) is the minimum distance from a rod to the z-axis, the inscribed radius of a system like the one defined in Figure 4-1. The voltages \([V]\) \( V_{0p} \) and \( U_a \) were introduced for Eq 4.12. Figure 4-2 illustrates the potentials in Eq 4.19/4.20.

The 0-to-peak amplitude, \( V_{0p} \), represents the periodic potential maximum amplitude, \( V_{0p}\cos(0) – V_{0p}\cos(\pi/2) \). The peak-to-peak amplitude, \( V_{pp} \), is the maximum potential difference reached over one cycle, \( V_{0p}\cos(0) – V_{0p}\cos(\pi) \), and the maximum potential difference between x- and y-rods at cycle peak. Likewise, if the quadrupole base potential is \( U \) (Eq 4.7, 4.11) then \( U_a \) is the potential offset of a rod as measured from \( U \) when the periodic potential is 0 and \( U'_a \) is the total offset between adjacent rods. Both conventions are used widely:
Eq 4.22  
\[ V_{pp} = 2 \cdot V_{0p} \; ; \; U'_a = 2 \cdot U_a \]

Making the substitution,

Eq 4.23  
\[ \xi = \frac{\alpha \cdot t}{2} \Rightarrow \frac{\partial^2 u}{\partial t^2} = \frac{\alpha^2}{4} \frac{\partial^2 u}{\partial \xi^2} \]

in Eq 4.14 and 4.15 leads to equations of the form,

Eq 4.24  
\[ \frac{\partial^2 u}{\partial \xi^2} + [a_2 - 2 \cdot q_2 \cdot \cos(2\xi)] \cdot u = 0 \]

This is the Mathieu differential equation of Eq 4.17 and 4.18. The properties of Eq 4.24 have been studied in great detail, only a few comments will follow. Detailed analyses of the solutions related to multi-pole instruments can be found in Pipes (1953), Pichanick (1967), Dawson (1976), Du et al. (1999), Sudakov (2001), Baranov (2003) and Baranov et al. (2005).

Floquet’s theorem can be used to solve for u in general, where u represents either x or y:

Eq 4.25  
\[ u = A \cdot e^{i \beta \xi} \sum_{s=-\infty}^{\infty} C_{2s} e^{2i\xi} + B \cdot e^{-i \beta \xi} \sum_{s=-\infty}^{\infty} C_{2s} e^{2i\xi} \]

The coefficients A and B are integration constants determined by initial \( \bar{u} \) and \( \frac{\partial u}{\partial t} \) in both x and y, and the \( C_{2s} \) coefficients and exponent \( \beta \) are determined by \( a_2 \) and \( q_2 \). When \( \beta \) is complex the series does not converge, corresponding to a trajectory with increasing amplitude. When \( \beta \) is real the series converges, representing stable trajectories in an ideal field, and Eq 4.25 can be expressed by a series of even and odd solutions:

Eq 4.26  
\[ u = A \sum_{s=-\infty}^{\infty} C_{2s} \cos(2s + \beta) \cdot \xi + B \sum_{s=-\infty}^{\infty} C_{2s} \sin(2s + \beta) \cdot \xi \]

Equation 4.26 describes ion oscillatory motion in the quadrupole field with amplitude \( C_{2s} \) at frequencies:

Eq 4.27  
\[ \Omega_s = |2s + \beta| \cdot \frac{\omega}{2} \]

where \( s \) is 0 or a positive or negative integer (March 1997 covers ion trap equivalents).

**4.1.1 Stability parameters in an ideal quadrupole field**

The integration constants A and B of Eq 4.26 influence overall oscillation amplitude and depend on initial ion position and velocity, and so also depend on initial ion kinetic energy. Conversely, \( \beta \) and the oscillation amplitude \( C_{2s} \) are functions of \( a_2 \) and \( q_2 \) and not the initial ion conditions or energy; they are determined by field properties and the ion m/q ratio. These
parameters determine the basic oscillation periods and dominant harmonics of ion motion.

The field oscillation frequency, $\omega$, affects stability through $q_2$ and $a_2$. To maintain constant $a_2$ and $q_2$ with higher $\omega$ requires larger potential offsets $V_{0p}$ (Eq 4.14/15) resulting in deeper potential wells and vice versa. Initial field phase can also affect the amplitude of a trajectory since it defines the initial strength and direction of the acceleration.

Application of an rf potential at one of the fundamental frequencies of an ion trajectory $\Omega_s$ (Eq 4.27) can cause the amplitude of the motion to get very large and lead to radial ion ejection from a quadrupole instrument.

While the $z$-trajectory does not affect the radial motion of ions in ideal quadrupole fields, it does affect the amount of time an ion will spend in a quadrupole field of finite length. In practical situations, ions that have trajectories with exponentially increasing amplitudes (‘unstable trajectories’) may nevertheless pass a quadrupole region if they do not undergo enough oscillations for radial ejection. The ‘length’ of an rf quadrupole region is often defined in terms of the number of rf cycles, $L_{rf}$, that ions experience. Assuming constant speed in the $z$-direction, if $K_z$ is the ion kinetic energy in the $z$-direction, $l$ is the physical length of the quadrupole region, and $f = \omega/2\pi$ is the rf frequency, then for an ion of mass $m$:

$$\text{Eq 4.28}$$

$$L_{rf} = \frac{\omega \cdot l}{2\pi} \cdot \sqrt{\frac{m}{2 \cdot K_z}} \cdot \left[ \frac{Hz \cdot m \cdot kg}{J} \right]$$

$$= 0.071987 \cdot f \cdot l \cdot \sqrt{\frac{m}{K_z}} \cdot \left[ MHz \cdot mm \cdot amu \right] \cdot \sqrt{\frac{amu}{eV}}$$

For quadrupole fields, $a_2$-$q_2$ stability diagrams can be constructed to determine where ion trajectories are stable in both $x$ and $y$ (shown in Appendix G). The first stability region along the $+q_2$-axis corresponds to $0 \leq \beta \leq 1$, $0 \leq a_2 < 0.24$, $0 \leq q_2 \leq 0.908047$. The second corresponds to $1 \leq \beta \leq 2$, $0 \leq a_2 < 0.03$ and $7.512 < q_2 \leq 7.58$.

Predominantly, only the first region is used, although use of the second region has been studied (Dawson and Bingqi 1984, Dawson 1986, Ying and Douglas 1996, Du et al. 1999, Zhao et al. 2009). While the second region is much narrower with more abrupt boundaries, the required higher voltages or rf frequencies, or combination, pose transmission challenges and produce more ‘rf heating’ (see section 4.1.2) on average. As mass filters, unwanted larger masses that have $q_2$ and $a_2$ stability in a lower region may pass, and as collision cells there may be unwanted additional energy in the centre-of-mass.
Figure 4-2 is a representation of one combination of potentials typically applied to an rf quadrupole instrument as described in Eq 4.7, 4.12 – 4.15 and sketched in Figure 4-1. A ‘rod offset potential’, U, may be applied to all four rods in order to change the relative potential with respect to other components in the system. Application of any voltage to the rods can affect ion trajectories through fringing fields and can cause axial ion acceleration.

Figure 4-2: Illustration of the Potential Offsets for an rf Quadrupole Instrument
Ions are confined by application of $V_0 \cos(\omega t)$. If only $U$ and $V_0 \cos(\omega t)$ are applied to the rods then $q_2 \neq 0$ and $a_2 = 0$. The rods produce a focusing field for half of the rf period and a defocusing field for the other half, $\pi$ out of phase so that while one rod pair produces a focusing field the other produces a defocusing field. In this situation, with $L_{nf}$ large enough and for operation in the first $q_2$ stability region (discussion after Eq 4.28), it is evident from Eq 4.19 that all ions above a threshold minimum mass (corresponding to $q_2 < 0.908$) will theoretically have stable trajectories. Instruments operated with $q_2 \neq 0$ and $a_2 = 0$ are known as ‘quadrupole ion guides’ and behave as high-pass mass filters.

On the other hand, if an additional potential $U_a$ is applied to one rod pair and $-U_a$ to the other then the baseline potential $U$ is effectively shifted by $U_a$ in each direction. In this case $q_2 \neq 0$ and $a_2 \neq 0$. Ions spend more time in a defocusing field in one direction and more time in a focusing field in the other direction, causing some ions that would have passed an ion guide to instead have unstable trajectories and be ejected from the system. Instruments operated with both $q_2 \neq 0$ and $a_2 \neq 0$ are known as ‘quadrupole mass filters’ and can be used to study mass spectra.

Both the numerator and denominator in Eq 4.19 and 4.20 have the units of energy. The denominator gives the angular energy that an ion of mass $m$ would have if it were in an orbit of radius $r_0$ at frequency $\omega$. Gerlich (1992 p. 35 eq. 50) and Litherland et al. (2009 p. 26) have called this a ‘characteristic energy’,

\[
\varepsilon_{ch} = \frac{m \cdot (r_0 \cdot \omega)^2}{2}
\]

Given this definition, the numerator then gives a characteristic potential energy. In the case of $q_2$.

\[
E_{cha2} = q \cdot V_{pp}
\]

(q is charge). This is the kinetic energy an ion would gain if it traversed the maximum possible potential difference between neighbouring rods (x- to y-rod), $V_{pp}$, and is the maximum potential energy between neighbouring rods at rf peaks and troughs. The stability parameter $q_2$ is then,

\[
q_2 = \frac{E_{cha2}}{\varepsilon_{ch}}
\]

For the first region of stability, the angular characteristic energy must be larger than the maximum potential energy between x- and y- rods. In a sense, rf quadrupole mass filters can be thought of as angular momentum filters. chapter 5 provides several examples of stable ion trajectories.
Calculation of $C_{2n}$ and $\beta$ is tedious and discussed at length in Dawson (1976 chapter III). For low values of $q_2$ (typically $\ll 0.4$) and $a_2$ there is a well-known approximation for $\beta$:

**Eq 4.32**

$$\beta = \sqrt{a_2 + \left( \frac{q_2^2}{2} \right)}$$

The ion trap equivalent is discussed in March (1997).

For large $q_2$ with systems operated as ion guides only ($a_2 = 0$), as $q_2$ approaches the upper stability boundary of the first region Sudakov (2001 p. 33 eq. 19) has calculated:

**Eq 4.33**

$$\lim_{q_2 \to 0.908047} \beta = 1 \sqrt{\frac{0.908047 - q_2}{1.39869}}$$

The parameters $q_2$ and $a_2$ can be generalized for multi-pole fields of order $n$ (as defined for Eq 4.1 – 4.4),

**Eq 4.34**

$$q_n = n \cdot (n-1) \cdot \frac{q}{m} \cdot \frac{V_{pp}}{\omega^2 r_0^2}$$

**Eq 4.35**

$$a_n = 2n \cdot (n-1) \cdot \frac{q}{m} \cdot \frac{U''}{\omega^2 \cdot r_0^2}$$

However, for $n > 2$ the stability boundaries are much less well-defined and these parameters do not define sharp cut-off regions of stability as they do for trajectories in quadrupole fields (discussed in Gerlich 1992 p. 41 – 45, Tanner et al. 2002 p. 1395 – 1397).

### 4.1.2 The Effective Potential $V^*$ and RF-Heating

Under adiabatic conditions in an rf quadrupole instrument the concept of an effective potential, $V^*(r)$, can be useful in describing ion behaviour. An in-depth analysis of $V^*(r)$ and its applicability to various situations can be found in Gerlich (1992). The name ‘effective potential’ is somewhat awkward because $V^*(r)$ actually has the units of energy, and is indeed expressed in electron volts, eV, throughout this thesis. It represents the average energy ‘stored’ in small oscillations that ions experience for lower $q_2$ trajectories.

Adiabatic conditions are satisfied when ions gain little energy from the rf field on average. The field is assumed to be decomposable into a static and an oscillatory term, and ion motion is separated into a slow secular motion, $\overline{R}_0(t)$, and a fast ‘wiggling’ oscillatory motion (see Figure 5-5), $\overline{R}_i(t)$, such that the trajectory can be written in the form:

**Eq 4.36**

$$\overline{r}(t) = \overline{R}_i(t) + \overline{R}_0(t)$$
The applied field is assumed to vary smoothly in $\mathbf{f}$ and have high enough frequency that the small oscillation amplitude of the ion is small enough that the ion does not experience large gradient changes during the wiggling. For this, Gerlich (1992 p. 19) introduced an adiabaticity parameter,

$$\eta = \frac{2 \cdot (\mathbf{a} \cdot \nabla^2) \cdot \mathbf{V}}{\nabla \mathbf{V}}$$  \hfill Eq 4.37

The effective potential (energy) represents the time-averaged effect of the oscillatory ion motion, $\mathbf{R}_i(t)$, in a field fluctuating with angular frequency $\omega$. For ion motion in rf multi-poles the effective potential may be written as:

$$V^*((r) = \frac{n^2}{16} \cdot \left( \frac{q \cdot V_{pp}}{m \cdot \omega^2 \cdot r_0^2} \right) \left( \frac{r}{r_0} \right)^{2n-2} + q \cdot \frac{U_{u}'}{2} \left( \frac{r}{r_0} \right)^n \cos(n\alpha)$$ \hfill Eq 4.38

$$= \frac{n}{(n-1)} \cdot \frac{q \cdot V_{pp}}{16} \cdot q_n \cdot \left( \frac{r}{r_0} \right)^{2n-2} + q \cdot \frac{U_{u}'}{2} \left( \frac{r}{r_0} \right)^n \cos(n\alpha)$$

The ion position is $r (r^2 = x^2 + y^2)$, $\tan \alpha = \frac{y}{x}$, and the other variables are described for Eq 4.19 – 4.22 (the subscripted $q_n$ represents the stability parameter, Eq 4.34, and the un-subscripted $q$ represents the charge of the ion). The effective potential has energy units and is proportional to $q^2$ so does not depend on the sign of the charge.

The adiabaticity parameter can be written (Gerlich 1992 p. 34),

$$\eta_n = n \cdot (n-1) \cdot \frac{q \cdot V_{pp}}{m \cdot \omega^2 \cdot r_0^2} \cdot \left( \frac{r}{r_0} \right)^{n-2} = q_n \cdot \left( \frac{r}{r_0} \right)^{n-2}$$ \hfill Eq 4.39

Maintaining $\eta_n \leq 0.3$ is a general rule for safe operation within the adiabatic approximation, although adiabaticity is possible for some larger values, even for $\eta_n > 0.6$. Under these conditions, kinetic energy fluctuations during ion motion are minimized and rf heating (discussed below) is reduced. For quadrupoles, the effective potential is often a useful approximation for $q^2 < 0.4$ (Gerlich 1992 p. 15, 20, 21). In the case of rf quadrupole ion guides, Eq 4.39 reduces to $q^2$ (Eq 4.19), independent of $r$, and

$$V^*(r) = \frac{q^2}{8} \cdot q \cdot V_{pp} \cdot \left( \frac{r}{r_0} \right)^2$$ \hfill Eq 4.40

$$V^*(r) \cdot [eV] = 0.0255728 \cdot q^2 \cdot m \cdot [amu] \cdot (r_0 [mm])^2 \cdot (f [MHz])^2 \cdot \left( \frac{r}{r_0} \right)^2$$
Under adiabatic conditions in rf multi-pole instruments it can be shown that,

Eq 4.41
\[
\frac{m}{2} \left( \frac{\partial R}{\partial t} \right)^2 + V^* = E_{ad}
\]

representing an adiabatic constant of ion motion (Gerlich 1992 p. 6 – 15). The transverse energy of an ion is conserved within narrow limits. Energy is exchanged between the effective potential arising from the small oscillatory motion, the smooth drift motion and, when present, an electrostatic potential.

In order to reduce this energy, a collision gas of lower average kinetic energy can be introduced for momentum transfer. Energy gained from an oscillating rf potential is known as ‘rf heat’. If ions are injected into a very strong region of the potential then the kinetic energy may be affected and the initial phase of the rf field may play a significant role in determining ion trajectories (discussed further in chapter 5).

Higher order multi-poles have effective potentials with much ‘steeper walls’ than lower order multi-poles, \( V^*(r) \propto \left( \frac{r}{r_0} \right)^{2(n-1)} \). The profiles for \( n = 2, 3, 4 \) and 5 are sketched in Figure 4-3. Away from the electrodes ions experience little acceleration for \( n > 2 \). The ‘small oscillations’ are most intense in rf quadrupole instruments and there is stronger confinement to the central region of the instrument where there is still significant interaction with the potential. This leads to more rf heating away from the electrodes, but also can lead to tighter ion beam confinement.

Limitations of the effective potential approximation in estimating rf heating are discussed in Baranov et al. (2005). Two dimensionless parameters that depend on \( a_2, q_2, \omega t \) and initial rf field phase (\( \theta \) in Eq 4.12 – 4.15) were derived for ion motion in quadrupoles and averaged over time and phase, \( v_{21}(a_2, q_2) \) and \( v_{22}(a_2, q_2) \) (Baranov 2004). Some tabulated values are copied in Appendix G. With these parameters, the average effect of the rf field of an rf quadrupole ion guide on ion energy can be expressed by:

\[
E_{rfad} = \frac{q \cdot V_{pp}}{4 \cdot q_2} \cdot \left[ \frac{r}{r_0} \right] \cdot v_{21}^2(0, q_2) + K_{rad} \cdot v_{22}^2(0, q_2)
\]

Eq 4.42
\[
= \frac{2 \cdot V^*(r)}{q_2^2} \cdot v_{21}^2(0, q_2) + K_{rad} \cdot v_{22}^2(0, q_2)
\]

Here (see Eq 4.19) \( q \) is the ion charge, \( q_2 \) is the rf quadrupole stability parameter, \( V_{pp} \) is the rf peak-to-peak voltage, \( r_0 \) is the rf quadrupole ‘inscribed radius’, \( r \) is the ion radial position, \( K_{rad} \) is
the ion radial kinetic energy, \( v_{21}(a_2, q_2) \) and \( v_{22}(a_2, q_2) \) are coefficients (tabulated values can be found in Appendix G), and \( V^*(r) \) is the effective potential (energy, Eq 4.40).

Intuitively, with \( q_2 \) held constant, rf heating increases with increasing \( V^*(r) \). This can be accomplished for all values of \( r(t) \) by increasing the applied rf potential and increasing the frequency while maintaining a constant ratio \( V_{pp}/\omega^2 \). Although this may produce low-\( q_2 \) stable trajectories, rf quadrupole instruments with larger applied voltages at higher frequencies are ‘hotter’.

Figure 4-3: Effective Potential \( V^*(r) \) for \( n = 2, 3, 4 \) and 5

The relative strength of the effective potential, \( V^* \) (Eq 4.38), for ion guide multi-poles of order \( n = 2 \) (quadrupole), 3 (hexapole), 4 (octopole) and 5 (decapole) are plotted versus ion position, \( r/r_0 \), in the multi-pole. The inscribed radius, \( r_0 \), is defined in Figure 4-1 and \( r^2 = x^2 + y^2 \).
Ion trajectories in an ideal rf quadrupole field are calculated in this chapter to understand some general features of transmission through an rf quadrupole ion guide of the design illustrated in Figure 4-1. The chapter is rather detailed and it would be sufficient for most readers to simply read the conclusions in sections 5.3.7 and 5.4.3.3.

A popular approach for calculating trajectories is based on a matrix method of approximate solutions to Eq 4.24 over set time intervals. Many of the general properties of the ion trajectory can be analysed while economizing the number of calculations. However, current computing power, costs and advances in applied mathematics have given rise to new approaches that allow more accurate analytical solutions that show features such as ‘small wiggling motions’ that are obscured with the matrix approach. A comparison is taken up in Baranov (2003).

Briefly, the present method uses Newton’s equations with the acceleration calculated using the Mathieu equations. Over small enough time steps (described in terms of the rf period) the acceleration and velocity can be approximated as constant, and a final position and velocity can be calculated from the initial conditions. This is similar to the matrix method except, as shown at Eq 5.4, the matrix method truncates velocity calculations so that they do not include a term accounting for acceleration, only initial position and initial velocity are used.

The present method does not consider fringing fields or ion-gas collisions. However, the simple modelling approach allows for addition of random collisions of arbitrary cross-section with arbitrary scattering angle and energy transfer very easily. A discussion of the matrix method is included due to its popularity and use in many of the cited references in this thesis, and for comparison to the approximations used herein.

5.1 A Matrix Approximation for Trajectory Analysis

Pipes (1953) described a general method of solution for Hill-Mathieu equations using a quasi-transfer matrix approach. Baril and Septier (1974) later elaborated the technique for determination of ion trajectories in rf quadrupole ion traps and showed the quasi-transfer matrices contained information about $\beta$ and phase space. A detailed step-by-step approach for rf quadrupole mass filters and ion guides can be found in Dawson (1974 and 1976) and Muntean (1995).
Fixing an appropriately small time interval $\Delta t$, Eq 4.17 and 4.24 may be combined as

$$G(\Delta t) = a_2 - 2 \cdot q_2 \cdot \cos \left[ 2 \cdot \left( \frac{\omega \cdot \Delta t}{2} - \xi_0 \right) \right],$$

where $\xi_0$ is the initial phase of the rf field. Let $G = \sqrt{G(\Delta t)}$ and $g = |G|$. Then the one-dimensional acceleration of an ion with a trajectory described by Eq 4.24 can be written as

**Eq 5.1**

$$\frac{\partial^2 u}{\partial t^2} = \pm g^2 \cdot u$$

It was shown that if $\begin{bmatrix} u & \dot{u} \end{bmatrix}_0^T (T\text{ is ‘transpose’, } 0 \text{ is ‘initial’})$ represents the initial ion position and velocity, and $\begin{bmatrix} u & \dot{u} \end{bmatrix}_1^T$ represents the position and velocity after $\Delta t$, then when $G = g$:

**Eq 5.2**

$$\begin{bmatrix} u & \dot{u} \end{bmatrix}_1 = \begin{bmatrix} \cos(g \cdot \Delta t) & g^{-1} \cdot \sin(g \cdot \Delta t) \\ -g \cdot \sin(g \cdot \Delta t) & \cos(g \cdot \Delta t) \end{bmatrix} \cdot \begin{bmatrix} u & \dot{u} \end{bmatrix}_0 = N_1 \cdot \begin{bmatrix} u & \dot{u} \end{bmatrix}_0$$

When $G = ig$, $\cos(ig) = \frac{e^{ig} + e^{-ig}}{2} = \frac{e^{-g} + e^g}{2} = \cosh(g)$ and $\sin(ig) = \frac{e^{ig} - e^{-ig}}{2i} = \frac{e^{-g} - e^g}{2i} = i\sinh(g)$, and Eq 5.2 becomes:

**Eq 5.3**

$$\begin{bmatrix} u & \dot{u} \end{bmatrix}_1 = \begin{bmatrix} \cosh(g \cdot \Delta t) & g^{-1} \cdot \sinh(g \cdot \Delta t) \\ g \cdot \sinh(g \cdot \Delta t) & \cosh(g \cdot \Delta t) \end{bmatrix} \cdot \begin{bmatrix} u & \dot{u} \end{bmatrix}_0 = N_2 \cdot \begin{bmatrix} u & \dot{u} \end{bmatrix}_0$$

Through an iterative process of matrix multiplication, position and velocity at any time $p \cdot \Delta t$ (p is an integer or 0) can be determined by multiplying the appropriate combination of $N_1$ and $N_2$ matrices for a total of $p$ multiplications. If representation of a full rf cycle were desired then $\Delta t$ should be chosen such that $p \cdot \Delta t = \frac{2\pi}{\omega}$ for some value of $p$, and the resulting 2x2 matrix would be a one cycle quasi-transfer matrix (squaring it would represent 2 cycles etc.).

In the limit $\Delta t \rightarrow 0$, or sufficiently small so that $g\Delta t \ll 1$, $\cos(g \cdot \Delta t) \approx \cosh(g \cdot \Delta t) \approx 1$ and $\sin(g \cdot \Delta t) \approx \sinh(g \cdot \Delta t) \approx g \cdot \Delta t$. Then Eq 5.2 and 5.3 may be written as,

$$u(\Delta t) \approx u_0 + \dot{u}_0 \cdot \Delta t$$

**Eq 5.4**

$$\dot{u}(\Delta t) \approx \dot{u}_0 \pm g^2 \cdot u_0 \cdot \Delta t = \dot{u}_0 + (G(\Delta t) \cdot u_0) \cdot \Delta t$$

where $(G(\Delta t) \cdot u_0)$ represents the acceleration of the ion (Eq 5.1). In this limit, Eq 5.4 yields a position according to Newtonian motion without accounting for acceleration, and a velocity according to Newtonian motion with constant acceleration.
5.2 Ion Trajectory Simulation Procedure

Calculations of ion trajectories in ideal rf quadrupole ion guide potentials were performed using MATLAB 7.0 – a mathematical programming software in which variables are stored as matrices. Iterative calculations were performed over fixed time-steps that were chosen to be small in comparison to a given rf frequency (discussed below), \( f = \frac{\omega}{2\pi} \). Solutions at each point were stored in a matrix representing a trajectory. With rf period \( T = \frac{1}{f} \),

Eq 5.5

\[ \Delta t = \frac{T}{\text{NumSteps}} \]

defined a time step where NumSteps represented the number of divisions per period. Equations 4.14/15 were used to calculate acceleration, \( a(t) \), expressed as:

Eq 5.6

\[ a_x(\Delta t \cdot p) = -\frac{\omega^2}{2} \cdot q_z \cdot \left[ \cos\left(2\pi \cdot \Delta t \cdot p - \theta \right) \right] \cdot x(\Delta t \cdot p) \]

\[ a_y(\Delta t \cdot p) = -\frac{\omega^2}{2} \cdot q_z \cdot \left[ \cos\left(2\pi \cdot \Delta t \cdot p - \theta \right) \right] \cdot y(\Delta t \cdot p) \]

Represented by \( p \) was the integer number of elapsed iterations so that at \( p \) a total elapsed time could be represented by \( t = \Delta t \cdot p \), \( \theta \) was an initial rf phase, and \( x(\Delta t \cdot p) \) and \( y(\Delta t \cdot p) \) represented the x and y position of the ion at time \( t \).

Initial and final accelerations in x and y were calculated according to Eq 5.6 at \( t_i = \Delta t \cdot (p - 1) \) and \( t_f = \Delta t \cdot p \), and used to determine a velocity at time \( t_f \) according to,

Eq 5.7

\[ v_{x,y}(t_f) = v_{x,y}(t_i) + \frac{[a_{x,y}(t_i) + a_{x,y}(t_f)]}{2} \cdot \Delta t \]

Displacements in x and y, \( dx \) and \( dy \), were then calculated by,

Eq 5.8

\[ dx, dy(t_f) = v_{x,y}(t_i) \cdot \Delta t + \frac{1}{2} \cdot a_{x,y}(t_i) \cdot \Delta t^2 \]

and a final position was determined by,

Eq 5.9

\[ x(t_f), y(t_f) = x(t_i), y(t_i) + dx(t_f), dy(t_f) \]

Ions were assigned a mass, \( m \), initial position, \( x(0) \) and \( y(0) \), and initial radial kinetic energy, \( K_r(0) = K_x(0) + K_y(0) \), and velocity direction unit vector,

Eq 5.10

\[ \text{dir}_{x,y}(0) = \frac{v_{x,y}(0)}{|v_{x,y}(0)|} = \pm 1 \]

so that an initial velocity was assigned (see Appendix A),
Mass affects the initial radial and z-axis velocities given \( K_r(0) \) and \( K_z(0) \), and would affect centre of mass energy during collisions, but only affects Eq 5.6 through \( q_2 \). The form and quasi-periodic nature of a particular \( q_2 \)-valued trajectory is general for any mass although the trajectory amplitude and the ion dwell time in an RF quadrupole instrument will depend on mass for a given set of \( K_r(0) \) and \( K_z(0) \).

With \( m \), \( r_0 \) and \( q \) constant, \( q_2 \) is modified by changing the magnitude of the potential that ions experience \( (V_{0p}) \) and by adjusting the amount of time that ions spend in focussing or defocussing phases of the RF potential \( (\omega) \). The quadrupole field was given a frequency, \( f \), and phase, \( \theta \), the instrument was assigned an inscribed radius, \( r_0 \) (Figure 4-1), and the system was given a \( q_2 \) value. No RF amplitude voltage was assigned, but it was implicitly defined through Eq 4.19. Fundamentally, \( q_2 \) was scanned by an implicit scan of \( V_{0p} \) since \( m \), \( q \), \( r_0 \) and \( \omega \) were held fixed throughout a given series of calculations over a range of \( q_2 \). This is the method of \( q_2 \) scanning for the current ISA. It is convenient in this case to use the second form of Eq 4.40 to calculate \( V^*(r) \).

Ions were considered ejected from the system when the radial position exceeded \( r_0 \),

\[
\text{Eq 5.12} \quad \text{Ion Ejection Criterion} \quad x^2 + y^2 \geq r_0^2
\]

Strictly speaking, such an ion might not be ejected from a physical system if it were between quadrupole rods. Some standard settings used throughout were,

<table>
<thead>
<tr>
<th>Table 5.1: Global Simulation Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f = \omega/2\pi = 2.6 \text{ MHz} )</td>
</tr>
<tr>
<td>( r_0 = 6.5 \text{ mm} )</td>
</tr>
</tbody>
</table>

Both \( f \) and \( r_0 \) correspond to ISA values and \( m \) was chosen to match the major Cl isotope.

5.2.1 Evaluation of Trajectory Simulation Time-Step

Trajectories for \( 0.1 \leq q_2 \leq 0.9 \) in steps of 0.05 with \( r_0 \), \( m \), \( q \) and \( \omega \) constant \( (V_{0p} \text{ scan}) \) were calculated to evaluate the validity of NumSteps = 1000 and are plotted in Figure 5-1 and 5-2. The absolute change during any step, \( |dx,y(t)| \), should be small compared to \( r_0 \). Also, the relative change during one iteration (length \( \Delta t \)), \( |dx,y(t)/dx,y(t+\Delta t)| \), while not constant for non-linear curves, should be minimized while maintaining reasonable processing times.
Trajectories were calculated with \( \theta = 0 \) for an ion in a ‘diverging beam’ – both \( v_x(0) \) and \( v_y(0) \) were chosen in a direction away from the z-axis. Under these conditions, the initial y-velocity was in the same direction as the initial acceleration while the initial x-velocity was in a direction opposite to the initial acceleration (Eq 5.6). The initial radial kinetic energy in both directions was \( K_{x,y}(0) = 1 \text{eV} \), the largest value used during simulations. All ions started at \( |x,y(0)| = 0.15r_0 \), representing a 1.4 mm radius. Calculations were done for \( L_{n_{\text{rf}}} = 60 \) rf cycles (Eq 4.28, eg. \( K_z = 2.77 \text{ eV} \) for \(^{35}\text{Cl}^- \) ions in a 15 cm long rf quadrupole instrument), and repeated using \( 2\omega \). Results for trajectories using \( \omega \) are shown in Figure 5-1 and Figure 5-2, the results using \( 2\omega \) were similar but with different amplitudes.

Under these conditions the \( q_2 = 0.9 \) trajectories, although theoretically quasi-periodic, were not stable in the sense of Eq 5.12 as ions were ejected before reaching \( L_{n_{\text{rf}}} \) (for both \( \omega \) and \( 2\omega \)). Ejection criterion Eq 5.12 was then modified to \( x^2(t) + y^2(t) < 2 \cdot r_0^2 \). With NumSteps = 1000, there were 60000 iterations per trajectory with the exception of \( q_2 = 0.9 \) since the radial position still exceeded the ejection criterion before \( L_{n_{\text{rf}}} \). Also shown is a trajectory that was stable according to Eq 5.12 for \( q_2 = 0.9 \) and \( \omega \), but with \( |x(0),y(0)| = 0.05r_0 \) representing a radius of 0.46 mm. The effect of initial position on trajectory amplitude is discussed later in this chapter.

Table 5.2 and Table 5.3 summarize the calculation variations over each iteration step. For more than 99.999% of the \( dx,dy \) calculated, \( dx,dy(t) \leq 2dx,dy(t+\Delta t) \), and for all calculations \( dx,dy(t) \leq 3dx,dy(t+\Delta t) \). The absolute increase for any given calculation, was also small compared to \( r_0 \), with no \( |dx,dy(t)| > 1\% \ r_0 \) and \( |dx,y(t)| > 0.1\% \ r_0 \) only for \( q_2 > 0.70 \).

**Caption for Figures 5-1 and 5-2**

Initial conditions: \( x(0) = -y(0) = 0.15r_0; \ \text{dir}_{x,y} = +1,-1 \) (Eq 5.10); \( K_{x,y}(0) = 1 \text{ eV} \) \( (K_z(0)= 2\text{ eV}) \); \( L_{n_{\text{rf}}} = 60 \) (Eq 4.28); \( \theta = 0 \); else as in Table 5.1. Plotted are trajectories in the x- and y- directions (see Figure 4-1) versus number of elapsed rf periods \( (\omega t/2\pi) \) for various \( q_2 \)-values (listed within each plot). Black curves represent \( x(t)/r_0 \) and red curves represent \( y(t)/r_0 \) and axes are identically scaled except for \( q_2 = 0.9 \). Trajectories were calculated according to Eq 5.5 – 5.11 using \( x^2(t) + y^2(t) < 2 \cdot r_0^2 \) as a modified ejection criterion (Eq 5.12). Under these conditions the \( q_2 = 0.9 \) trajectory was not stable, but setting \( x(0) = -y(0) = 0.05r_0 \) yielded a trajectory stable according to Eq 5.12 (shown in Figure 5-2). Using Eq 4.27 to calculate the base oscillation frequency, \( \Omega_0 \), the ‘secular’ periods \( (T_0) \) of low-\( q_2 \) trajectories are well approximated using Eq 4.32, discussed in the next section.
Figure 5-1: Trajectory Simulation Plots X(t) v. t and Y(t) v. t for 0.1 ≤ q_2 ≤ 0.5 for an Ideal rf-Quadrupole Field (see p. 5—40 for caption)
Figure 5-2: Trajectory Simulation Plots $X(t)$ v. $t$ and $Y(t)$ v. $t$ for $0.55 \leq q_2 \leq 0.9$ for an Ideal rf-Quadrupole Field (see p. 5-40 for caption)
Table 5.2: Evaluation of Time Step $\Delta t$ for NumSteps = 1000 (for $\omega$)

<table>
<thead>
<tr>
<th>$q_2$</th>
<th>Rate of Change of Increase</th>
<th>Absolute Increase</th>
<th>Iterations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$dx, y(t) / dx, y(t + \Delta t)$</td>
<td>$dx, y / r_0$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&gt; 2</td>
<td>&gt; 3</td>
<td>&gt; 0.001</td>
</tr>
<tr>
<td></td>
<td>$x$</td>
<td>$y$</td>
<td>$x$</td>
</tr>
<tr>
<td>0.10</td>
<td>192</td>
<td>192</td>
<td>1</td>
</tr>
<tr>
<td>0.15</td>
<td>93</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>0.20</td>
<td>114</td>
<td>138</td>
<td>0</td>
</tr>
<tr>
<td>0.25</td>
<td>119</td>
<td>166</td>
<td>1</td>
</tr>
<tr>
<td>0.30</td>
<td>103</td>
<td>137</td>
<td>0</td>
</tr>
<tr>
<td>0.35</td>
<td>114</td>
<td>145</td>
<td>1</td>
</tr>
<tr>
<td>0.40</td>
<td>129</td>
<td>91</td>
<td>1</td>
</tr>
<tr>
<td>0.45</td>
<td>236</td>
<td>211</td>
<td>1</td>
</tr>
<tr>
<td>0.50</td>
<td>161</td>
<td>134</td>
<td>1</td>
</tr>
<tr>
<td>0.55</td>
<td>176</td>
<td>93</td>
<td>2</td>
</tr>
<tr>
<td>0.60</td>
<td>92</td>
<td>99</td>
<td>1</td>
</tr>
<tr>
<td>0.65</td>
<td>77</td>
<td>73</td>
<td>1</td>
</tr>
<tr>
<td>0.70</td>
<td>65</td>
<td>76</td>
<td>2</td>
</tr>
<tr>
<td>0.75</td>
<td>73</td>
<td>32</td>
<td>1</td>
</tr>
<tr>
<td>0.80</td>
<td>33</td>
<td>28</td>
<td>2</td>
</tr>
<tr>
<td>0.85</td>
<td>48</td>
<td>55</td>
<td>1</td>
</tr>
<tr>
<td>0.90</td>
<td>3</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

Initial conditions: $x(0) = -y(0) = 0.15r_0$; $\text{dir}_{x,y} = +1, -1$; $K_{x,y}(0) = 1 \text{ eV}$; $\text{Ln}_t = 60$; $\theta = 0$; else as in Table 5.1; see Eq 5.5 – 5.11. Equation 5.12 was modified so that when $x^2(t) + y^2(t) < 2 \cdot r_0^2$ ions were considered ejected and calculation stopped. For all $q_2$ trajectories the rate of change of position for more than 99.999% of the iterations was $\leq 2$ and there were no cases of quadrupling the displacement $dx, y(t + \Delta t)$ relative to $dx, y(t)$ (not shown). The absolute increase for all $q_2 \leq 0.70$ was less than 0.1% $r_0$. No increases were greater than 1% $r_0$, including for trajectories with $q_2 = 0.9$ where ions were ejected. Areas of larger increase were not clustered late in the data. Trajectories are plotted in Figure 5-1 and Figure 5-2.
Table 5.3: Evaluation of Time Step \( \Delta t \) for NumSteps = 1000 (for \( 2\omega \))

<table>
<thead>
<tr>
<th>( q_2 )</th>
<th>Rate of Change of Increase</th>
<th>Absolute Increase</th>
<th>Iterations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \frac{dx, y(t)}{dx, y(t + \Delta t)} )</td>
<td>( \frac{</td>
<td>dx, y</td>
</tr>
<tr>
<td></td>
<td>( &gt; 2 )</td>
<td>( &gt; 3 )</td>
<td>( &gt; 0.001 )</td>
</tr>
<tr>
<td>x</td>
<td>y</td>
<td>x</td>
<td>y</td>
</tr>
<tr>
<td>0.10</td>
<td>182</td>
<td>209</td>
<td>0</td>
</tr>
<tr>
<td>0.15</td>
<td>297</td>
<td>294</td>
<td>1</td>
</tr>
<tr>
<td>0.20</td>
<td>285</td>
<td>284</td>
<td>0</td>
</tr>
<tr>
<td>0.25</td>
<td>286</td>
<td>254</td>
<td>1</td>
</tr>
<tr>
<td>0.30</td>
<td>211</td>
<td>233</td>
<td>1</td>
</tr>
<tr>
<td>0.35</td>
<td>204</td>
<td>184</td>
<td>1</td>
</tr>
<tr>
<td>0.40</td>
<td>161</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>0.45</td>
<td>111</td>
<td>222</td>
<td>1</td>
</tr>
<tr>
<td>0.50</td>
<td>99</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>0.55</td>
<td>66</td>
<td>103</td>
<td>2</td>
</tr>
<tr>
<td>0.60</td>
<td>63</td>
<td>89</td>
<td>0</td>
</tr>
<tr>
<td>0.65</td>
<td>49</td>
<td>78</td>
<td>3</td>
</tr>
<tr>
<td>0.70</td>
<td>63</td>
<td>56</td>
<td>1</td>
</tr>
<tr>
<td>0.75</td>
<td>59</td>
<td>52</td>
<td>1</td>
</tr>
<tr>
<td>0.80</td>
<td>55</td>
<td>94</td>
<td>1</td>
</tr>
<tr>
<td>0.85</td>
<td>38</td>
<td>52</td>
<td>0</td>
</tr>
<tr>
<td>0.90</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Initial conditions: \( x(0) = -y(0) = 0.15r_0 \); \( \text{dir}_{x,y} = +1, -1 \); \( K_{x,y}(0) = 1 \text{ eV} \); \( \text{L}_{x,y} = 60 \); \( \theta = 0 \); else as in Table 5.1 except using \( 2\omega \) \((2f = 5.2 \text{ MHz})\); see Eq 5.5 – 5.10. When \( x^2(t) + y^2(t) < 2 \cdot r_0^2 \), ions were considered ejected and calculation stopped. For all \( q_2 \) trajectories the rate of change of increase for more than 99.9994% of the iterations was \( < 2 \) and there were no cases of quadrupling the displacement \( dx, y(t + \Delta t) \) relative to \( dx, y(t) \) (not shown). The absolute increase was less than 0.1% \( r_0 \) for all \( q_2 \), including for trajectories with \( q_2 = 0.9 \) where ions were ejected. Areas of larger increase were not clustered late in the data.
5.3 General rf Quadrupole Ion Guide Ion Trajectory Characteristics

In this section some general properties of ion trajectories in rf quadrupole ion guides are studied in order to understand optimum design characteristics and current transmission losses for the ISA system. During a given set of calculations spanning a range of \( q_2 \) the variables \( m, r_0, q \) and \( \omega \) were held constant so that \( q_2 \) was scanned implicitly by scanning \( V_{0p} \). Currently this is the method of operation for the ISA.

5.3.1 General Properties

Plots showing two-dimensional projections of the radial motion for the trajectories in Figure 5-1 and Figure 5-2 are shown in Figure 5-3 (except for \( q_2 = 0.9 \)). For low \( q_2 \) the projection is fairly linear in the central region. As the radial position increases, the ion enters regions where the rf field goes through larger maxima and minima and ion motion is more strongly coupled with the applied rf voltage. Ions are more strongly attracted to and deflected from the rods, executing a ‘wiggle’ motion before finally being deflected back towards the central region where motion returns to a more linear path. ‘Wiggles’ for low \( q_2 \) x-motion can be seen in Figure 5-5.

As \( q_2 \) increases, the small oscillations grow, extending further towards the central region. The projections broaden as ions are attracted more strongly to the x- and y-rods and larger \( q_2 \) projections resemble ‘squares’ rather than ‘rectangles’, peaking at \( (x,y) = \{ \pm r_0, 0; 0, \pm r_0 \} \) where ions are closest to the rods. Factors affecting the amplitudes of oscillation in x and y separately are discussed later in this chapter. The projections are ‘hollow’, the central ‘hole’ resulting from conservation of angular momentum as noted by Gerlich (1992).

Figure 5-4 presents several of the projections superimposed to illustrate the relative scale of the trajectory path length. Larger \( q_2 \) trajectories can result in longer ion paths through a quadrupole instrument which would lead to more collisions on average in the presence of a gas, and also result in more rf heating (Eq 4.42). The radial trajectories are broader for larger \( q_2 \) which could lead to larger transmission losses if apertures were present. Likewise, although not broad, lower \( q_2 \) trajectories can have large radial amplitude resulting in transmission losses in the presence of apertures. Given a finite \( L_{dr} \) for the ISA, rf heating, trajectory amplitude and path-length must all be considered in order to maximize isobar separation, minimize unwanted reactions and maximize transmission through gas-restricting apertures.
Figure 5-3: 2-D Projections of Trajectory Position $X(t)$ v. $Y(t)$ for $0.1 \leq q_2 \leq 0.9$ for an Ideal rf Quadrupole Field (see p. 5-48 for caption)
Figure 5-4: Relative Scale of 2-D Trajectory Projections for X(t) vs. Y(t) (see p. 5—48 for caption)
Captions for Figure 5-3 and Figure 5-4

Figure 5-3: The trajectories from Figure 5-1 and Figure 5-2 are re-plotted to show x(t)/r₀ vs. y(t)/r₀ (x and y normalized to the ‘inscribed radius’, Figure 4-1). Given the conditions listed for Figure 5-1 and Figure 5-2, these plots represent a two-dimensional projection of the idealized x-y motion of an ion in an ideal rf quadrupole ion guide. Axes are not identically scaled however individual plots are all on square grids. The ‘hole’ in the middle of each plot arises from conservation of angular momentum. Factors affecting the differences in x and y trajectory maxima are discussed later in this chapter.

Figure 5-4: Several plots from Figure 5-3 are superimposed to show the relative cross-sectional areas covered by an ion for different q₂ trajectories (initial conditions from Figures 5–1 and 5–2). Both x(t) and y(t) are normalized to the ‘inscribed radius’, r₀, as in Figure 5-3, and r₀ is shown as a dashed line. Quadrupole rods would be closest to the z-axis (Figure 4-1) at (x,y) = {±r₀,0; 0,±r₀}. Given the same initial conditions, trajectories are more linear for lower q₂ but broaden as q₂ gets larger due to the increasing field gradients. At larger q₂, trajectories are distorted towards (x,y) = {±r₀,0; 0,±r₀} where the rf fields reach maxima.

5.3.2 Oscillation Frequency and Period

Trajectory oscillation frequencies are described by Ωₙ (Eq 4.27), with the dominant frequency at s = 0 in ideal rf quadrupole fields. From Figure 5-1, for low q₂ values (especially q₂ ≤ 0.30), ion motion appears to consist of a fast ‘wiggling’ motion superimposed on a slow secular motion as was posited for the effective potential approximation (Eq 4.36) and discussed for the projections in Figure 5-3. As q₂ increases ions pass through a larger potential difference during a half period of ω. The small motions become more exaggerated and finally become large motions of the trajectory. On the other hand, as discussed by Sudakov (2001), the oscillations appear contained in an envelope and a beat motion becomes apparent at large q₂ (Figure 5-2).

Using Eq 4.27 and 4.32 a dominant period can be calculated for low q₂,

\[ T_0(\omega) \equiv \frac{T_0}{T_\omega} = \frac{\omega}{\Omega_0} = 2\sqrt{2}\frac{1}{q_2} \]

while for q₂ → 0.908047, β → 1 (Eq 4.33) and Ω₀ → ω/2 so that

\[ T_0(\omega)_{q_2 \rightarrow 0.908047} \rightarrow 2 \]

T₀(ω) is the number of periods of ω required for one period of Ω₀. The trajectory periods in Figure 5-1 (q₂ ≤ 0.5) are compared to Eq 5.13 in Table 5.4. For q₂ > 0.35, Eq 5.13 becomes less accurate at describing the long (‘secular’) period of motion as expected.

Figure 5-5 shows several trajectories in the x-direction for 0.1 < q₂ < 0.2 over Ln₁rf = 30. Periods T₀(ω) are well described by Eq 5.13 as expected. The small wiggling motions are in phase with ω and have the same period. This type of situation was also posited for the effective
The major trajectory period is in units of rf periods, $2\pi/\omega$. It was calculated using Eq 5.13 and compared to the period as measured from the trajectories in Figure 5-1. As $q_2$ gets larger Eq 5.13 becomes less accurate.

Table 5.4: Measured vs. Calculated Major Periods for Low $q_2$ Trajectories

<table>
<thead>
<tr>
<th>$q_2$</th>
<th>0.10</th>
<th>0.15</th>
<th>0.20</th>
<th>0.25</th>
<th>0.30</th>
<th>0.35</th>
<th>0.40</th>
<th>0.45</th>
<th>0.50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major Period</td>
<td>Calculated</td>
<td>28.28</td>
<td>18.86</td>
<td>14.14</td>
<td>11.31</td>
<td>9.43</td>
<td>8.08</td>
<td>7.07</td>
<td>6.29</td>
</tr>
<tr>
<td>$[\omega/\Omega_0]$</td>
<td>Figure 5-1</td>
<td>28.18</td>
<td>18.76</td>
<td>14.16</td>
<td>11.33</td>
<td>9.29</td>
<td>8.07</td>
<td>6.91</td>
<td>6.03</td>
</tr>
</tbody>
</table>

potential approximation (Gerlich 1992). Comparing Figure 5-5 to Figure 5-3, low $q_2$ trajectories essentially consist of a linear drift near the central region.

Figure 5-6 shows an expanded section of the $q_2 = 0.9$ trajectory that remained confined according to criterion Eq 5.12 shown in the last panel of Figure 5-2. Ions oscillate according to an envelope ‘beat motion” within which the oscillation period is twice the period of $\omega_0$, consistent with Eq 5.14. Every oscillation in x or y crosses the x- or y-axis and there is no apparent small wiggle at the peaks away from the beat nodes.

In general, the small ‘wiggling’ motion has a period of $2T_\omega$ and occurs when ions are in regions of the rf field where the gradients are strong enough to cause a relatively immediate ion response to changes in the field. At peak voltage, one set of rods strongly attracts the ions while the other strongly repels them. As seen in Figure 5-3, in such regions ions move to and from the rods, and this shows up as wiggles in x- and y-trajectory plots. Then, $2T_\omega$ represents 2 full cycles of maxima on the rods needed for the ions to move in the directions of one set of rods, be repelled, move to the other set, and then be repelled again. As $q_2$ increases, the gradients increase until they are strong enough to cause such ion response throughout the motion and finally the dominant period approaches $2T_\omega$ for $q_2 = 0.9$.

5.3.3 Initial Position and Kinetic Energy

The maximum amplitude of a trajectory is affected by both the rf field conditions and the initial conditions of ion motion such as radial kinetic energy $K_r(0)$ and position $r(0)$. Already in Figure 5-2, $r(0)$ was shown to affect the trajectory amplitude for $q_2 = 0.9$. Under the given conditions, when $r(0) = 0.21r_0$ ions were confined within $\sqrt{2 \cdot r_0}$ for only $L n_{rf} < 4$ while setting $r(0) = 0.07r_0$ led to ion confinement within a radius of $r_0$ (Eq 5.12) indefinitely.
Figure 5-5: Small Oscillations for X-Motion $0.10 \leq q_2 \leq 0.20$ – Low $q_2$ ‘Wiggle’ Motion

Initial conditions: $x(0) = -y(0) = 0.05r_0$, $x(0) = 0.07r_0$; $\text{dir}_{x,y} = +1, -1$ (Eq 5.10); $K_{x,y}(0) = 1$ eV ($K_y(0) = 2$ eV); $\text{Ln}_{rf} = 30$ (Eq 4.28); $\theta = 0$; else as in Table 5.1. Trajectories were calculated according to Eq 5.5 – 5.11 using ejection criterion Eq 5.12. Plotted are trajectories in the x-direction (see Figure 4-1) versus number of elapsed rf periods ($\omega t/2\pi$) for various $q_2$-values. The top axis shows the actual rf phase and the bottom axis shows the number of elapsed rf periods. Trajectories appear to consist of a fast ‘wiggling’ motion, in phase with $\omega$ and with the same period, superimposed on a slower ‘secular’ motion. Using Eq 5.13 to calculate the base oscillation frequency, $\Omega_0$, the ‘secular’ periods ($T_0$) of low-$q_2$ trajectories are well approximated.
This is an expanded view of a ‘beat envelope’ for the $q_2 = 0.9$ with $x(0) = -y(0) = 0.05r_0$ trajectory in Figure 5-2 (see caption for initial conditions). The shorter-period oscillations away from the ‘envelope nodes’ correspond to $T_0(\omega) \approx 2 \cdot T_0$, as predicted by Eq 5.14. There is no apparent ‘small wiggle’ motion away from the nodes as there is for low $q_2$ trajectories (eg. Figure 5-5), now the ‘wiggles’ have become major oscillations.

In general, ions that enter the field further from the z-axis effectively enter a region of larger initial potential energy that can be converted into kinetic energy, leading to larger trajectory amplitudes. Under the same conditions, ions with greater $K_r(0)$ will also have larger amplitude trajectories. Often for $q_2 \geq 0.25$, $E_{ad} > K_r(0) + V'(r(0))$ (Eq 4.41) is found to hold.

The effects of $r(0)$ and $K_r(0)$ are compared in Figure 5-7 for $q_2 = 0.3$, $K_r(0) = 2$ eV and 0.05 eV and $r(0) = 0.21r_0$ and 0.07$r_0$. Both $v_{x,y}(0)$ are directed towards the z-axis as for an ion in a ‘converging’ beam. Initial direction and rf phase effects are discussed below, but it should be noted that these results are general. In all cases $V'(r) > K_r(0) + V'(r(0))$ was required for ion confinement within $r(t) < r_0$, and $r(0)$ and $K_r(0)$ affected trajectory amplitude dramatically.
Figure 5-7: Influence of Initial Position and Kinetic Energy on Trajectory Amplitude

Initial ion and rf field conditions correspond to Table 5.1 and $q_2 = 0.3$; $x(0) = -y(0) = 0.15r_0$ ($r(0) = 0.21r_0$) or $0.05r_0$ ($r(0) = 0.07r_0$); $K_{x,y}(0) = 1\text{eV}$ ($K_r(0) = 2\text{eV}$) or $0.025\text{eV}$ (Thermal, $K_r(0) = 0.05\text{eV}$); $\text{dir}_x = -\text{dir}_y = -1$; $\theta = 0$.

Plotted is the ion radial position versus the driving rf quadrupole field phase, $\omega t$. Ions that begin further from the $z$-axis effectively have more potential energy from the rf field and have larger amplitudes. Larger $K_r(0)$ also yields larger amplitude trajectories. All radial trajectories exceed $V^*(r) = K_r(0) + V^*(r(0))$, where $V^*(r)$ is the effective potential (Eq 4.40). Differences in $K_r(0)$ and $r(0)$ can be seen to produce dramatically different trajectory amplitudes.

Figure 5-8 and Figure 5-9 compare radial amplitudes for the trajectories in Figure 5-1 and Figure 5-2 to trajectories under the same conditions but with 1/3 the initial position. In both cases $K_r(0) = 2\text{eV}$ ($K_{x,y}(0) = 1\text{eV}$) and a green “dash-dot-dash” line is included for $q_2 \leq 0.5$ to indicate $V^*(r) = 2\text{eV}$. In all cases a minimum of $2\text{eV}$ is required for ion confinement and ions starting further from the $z$-axis attain larger radial amplitudes, require a greater effective potential for confinement (Eq 5.12), and so would be subject to greater rf heating (Eq 4.42). As $q_2$ is increased, differences in $r(0)$ have an even greater impact on relative trajectory amplitudes.
Figure S8: Comparison of Two Initial Positions on Trajectory Amplitude for $0.1 \leq q_2 \leq 0.5$ (see p. 5-55 for caption)
Figure 5-9: Comparison of Two Initial Positions on Trajectory Amplitude for $0.55 \leq q_2 \leq 0.9$ (see p. 5-55 for caption)

$r(t)/r_0 \quad (r(0)=0.21r_0; \quad r(0)=0.07r_0)$

Number of Elapsed rf Periods ($\omega t/2\pi$)

rf Phase ($\omega t$)
Captions for Figure 5-8 and Figure 5-9

Radial amplitudes for the trajectories in Figure 5-1, Figure 5-2 (r(0) = 0.21r₀) are compared to those for trajectories with r(0) = 0.07r₀ but otherwise identical conditions (see caption for Figure 5-1 Figure 5-2). Position axis (r(t)/r₀) scales are consistent across rows but vary down columns. Trajectories with larger r(0) have larger amplitudes since ions gain more potential from the rf field initially, and the difference gets more dramatic for larger q₂ trajectories. The green ‘dash-dot-dash’ indicates V*(r) = 2eV. For q₂ ≥ 0.25, V'(r) > Kᵣ(0) + V'(r(0)) is attained.

5.3.4 Initial rf Phase

The initial phase of the rf field, θ, affects the magnitude and sign of initial acceleration. Discussion will be restricted mainly to q₂ ≤ 0.35 where the effective potential approximation is valid and T₀(ω)/4 > 2T₀, the present range of concern for the ISA as a cooler and reactor.

For θ = 0 (Eq 5.6), x-trajectories undergo an initial – acceleration for a quarter period of ω and then experience a half period of + acceleration, and then alternating half periods of – and + accelerations. The reverse is true in the y direction (x and y fields are π out of phase), and the reverse in both directions is true for θ = π. Variations in θ lead to variations in trajectory maxima and these variations are less severe when ions are confined to regions of weaker rf potential, for example lower q₂, Kᵣ(0) and r(0).

Figure 5-10 illustrates the effect of θ on trajectory amplitudes for q₂ = 0.3 with Kₓ,y(0) = 1eV (Kᵣ(0) = 2eV) for r(0) = 0.21r₀ and 0.07r₀ and vₓ,y(0) directed away from the z-axis (‘diverging’). For all trajectories, ions experience V*(r) > 2eV. The range of maximum amplitudes attained over the range of θ is greatest for ions that begin at r(0) = 0.21r₀. Trajectory periods, T₀(ω), remain constant and are most tightly grouped for \( k \in \mathbb{Z} \) and most varied at the peaks, \( Ln_{rf} = \left( \frac{2k - 1}{4} \right) \cdot T₀(\omega) \).

A series of trajectories for q₂ = 0.3, Kₓ,y(0) = 1eV (Kᵣ(0) = 2eV), r(0) = 0.07r₀ with vₓ,y(0) directed away from the z-axis (‘diverging’) was calculated for Lnᵣ₉ = 30. The maximum x, y and radial amplitudes of each trajectory were used to calculate the maximum effective potential experienced by ions over 0 ≤ θ ≤ 2π in steps of Δθ = π/8. Results are presented in Figure 5-11. The asymmetry of aₓ and aᵧ (Eq 5.6) and the symmetry of the initial conditions in x and y can be seen in the maximum amplitudes attained in x and y over the range of θ, with maximum x(ot₁) ≈ maximum y(ot₁+π). For several values of θ, V*(x(₉)) < 1eV for all t, while at others V*(y(₉)) < 1eV for all t. However, V*(r) ≥ 2eV for all values of θ. Although ion motion in quadrupole rf fields is separable in x, y and z, not all properties can be considered separately.
Initial ion and rf field conditions correspond to Table 5.1 and $q_2 = 0.3$; $x(0) = -y(0) = 0.15r_0$ ($r(0) = 0.21r_0$) or $0.05r_0$ ($r(0) = 0.07r_0$); $K_{x,y}(0) = 1\text{eV}$ ($K_r(0) = 2\text{eV}$); $\text{dir}_x = \text{dir}_y = -1$. Plotted is the ion radial position, $r^2 = x^2 + y^2$, versus the driving rf quadrupole field phase, $\omega t$, for several values of the initial rf phase $\theta$ (Eq 5.6). Ions that begin further from the z-axis are most strongly affected by differences in $\theta$ and all radial trajectories enter regions of $V^*(r) > K_r(0)$, where $V^*(r)$ is the effective potential (Eq 4.40). Ion positions are most dispersed at the trajectory peaks and most tightly bunched for $r(t) = r(0)$. 

**Figure 5-10**: Influence of Initial rf Phase on Trajectory Amplitude for 2 Initial Positions
Figure 5-11: Maximum Effective Potential Experienced in x, y and r Coordinates vs. Initial rf Phase

Initial ion and rf field conditions correspond to Table 5.1 and $q_2 = 0.3$; $x(0) = -y(0) = 0.05r_0$ ($r(0) = 0.07r_0$); $K_{x,y}(0) = 1\text{eV}$ ($K_{r}(0) = 2\text{eV}$); $\text{dir}_x = -\text{dir}_y = -1$. Plotted is the maximum effective potential experienced by an ion in $x$, $y$ and $r$ versus the initial rf phase $\theta$ (Eq 5.6) for $\ln r_0 = 30$. The right axis ticks correspond to the effective potential while the left labels indicate the position at which $V^*(x, y, r)$ is attained. Since $V^*(x,y,r) \propto (x,y,r/r_0)^2$ the position scale is not linear. Although $K_{x,y}(0) = 1\text{eV}$, there are several values of $\theta$ for which ions do not experience $V^*(x,y) > 1\text{eV}$ over the trajectory. However, all ions experience $V^*(r) > 2\text{eV}$.

Figure 5-12 compares the effect of $\theta$ on maximum trajectory amplitude for $q_2 = \sqrt{2}/10$ and $q_2 = 0.3$ at different $K_r(0)$, plotting maximum $V^*(r)$ vs. $\theta$ and listing the maximum and minimum $r(0)/r_0$ attained. Variation in maximum amplitude is greater for the $q_2 = 0.3$ trajectories although they are confined to smaller $r(0)/r_0$. As discussed above, the lower $q_2$ trajectories are less affected by variations in $\theta$ than the larger $q_2 = 0.3$ trajectories and experience less rf heating. More energy is imparted to ions from the rf field for larger $q_2$ and there is more variation in rf heating over the full range of initial rf phases than for lower $q_2$. When conducting ion-gas
interaction experiments, especially for ion beams with large divergence or convergence, \( K_r(0) \) and \( r(0) \), using larger \( q_2 \) can confine the ion beam to a smaller radius but may lead to significant variations in centre of mass energy over the full range of \( \theta \). Using a lower \( q_2 \) leads to less rf heating and can minimize energy differences over \( \theta \), but trajectory amplitudes are larger so require larger apertures or more sophisticated focusing at apertures.

Figure 5-12: Maximum Effective Potential vs. Initial rf Phase for Various \( q_2 \) and \( K_r(0) \)

![Graph showing Maximum Effective Potential vs. Initial rf Phase for Various \( q_2 \) and \( K_r(0) \)](image)

Initial ion and rf field conditions correspond to Table 5.1 and \( q_2 = \sqrt{2}^{1/10} \) or 0.3; \( x(0) = -y(0) = 0.05r_0 \) (\( r(0) = 0.07r_0 \); \( \text{dir}_x = -\text{dir}_y = -1 \)). Plotted is the maximum effective potential experienced by an ion versus the initial rf phase \( \theta \) (Eq 5.6) with \( L_{\text{nf}} = 30 \) for various values of \( K_r(0) \) (\( K_{x,y}(0) = K_r(0)/2 \)). The legend gives the maximum and minimum position, \( r(t)/r_0 \), attained during the trajectory. All ions experience \( V'(r) > K_r(0) \). While ions are more tightly confined to the z-axis for \( q_2 = 0.3 \), they experience a stronger effective potential and so more rf heating over \( \theta \) than do ions for \( q_2 = \sqrt{2}^{1/10} \). A wider spread in rf heating accompanies the larger \( q_2 \) trajectories since there is a larger variation in \( V'(r) \) over \( \theta \).
Initial ion and rf field conditions correspond to Table 5.1 and $q_2 = 0.3$; $x(0) = -y(0) = 0.15r_0$ ($r(0) = 0.21r_0$); $K_{x,y}(0) = 1\text{eV}$ ($K_r(0) = 2\text{eV}$); $\theta = \pi/2$. Plotted are trajectories in x and y for two conditions: 'converging' in which both $v_x(0)$ and $v_y(0)$ are directed towards the z-axis, and 'diverging' in which they are both directed away from the z-axis. The right and left axis ticks show ion position with graduation values shown on the left axis. The values along the right axis indicate what the effective potential is at the marked positions, but the scale is not linear as $V^*(x,y) \alpha (x,y/r_0)^2$ (Eq 4.40). Changing $dir_{x,y}$ mainly affects the peak positions and has a small effect on trajectory amplitudes.

5.3.5 Initial Direction of Ion Motion – Converging vs. Diverging Motion

Initial velocity direction ($dir_{x,y}$ in Eq 5.10 and 5.11) can affect trajectory amplitude and effectively shift the positions of maxima and minima for a given initial rf phase ($\theta$, Eq 5.6). Figure 5-11 demonstrates a general result that trajectories in x and y can differ greatly in amplitude for most values of $\theta$, as is the case in Figure 5-1 – Figure 5-4 and Figure 5-6 for $\theta = 0$. Greater $q_2$ trajectories show greater differences. Figure 5-13 compares a ‘converging’ scenario where both $v_x(0)$ and $v_y(0)$ are directed toward the z-axis to a ‘diverging’ scenario where they are
both directed away from the z-axis for $q_2 = 0.3$, $K_r(0) = 2\text{eV}$ ($K_{x,y}(0) = 1\text{eV}$), $\theta = \pi/2$ and $x(0) = -y(0) = 0.15 r_0$. Radial amplitude is compared to the x and y trajectories in Figure 5-11 for $x(0) = -y(0) = 0.05 r_0$, results would be similar for trajectories with the initial conditions of Figure 5-13.

Because of the symmetry of the initial conditions and asymmetry of Eq 5.6, changing the direction of the initial velocity leads to a virtual exchange of the x and y trajectories and a shift in peak positions. Besides the direction of the initial acceleration, the initial conditions for x in the ‘converging’ scenario are the same as those for y in the ‘diverging’ scenario and vice versa. Because the initial acceleration in y is away from the z-axis while in x it is towards the z-axis, the peak maxima or minima are effectively delayed by the choice of $\text{dir}_{x,y}$, causing a shift in peak position. Trajectory form is mainly a function of the quadrupole stability parameters so is essentially unaffected by $\text{dir}_{x,y}$.

The radial trajectory amplitudes for a ‘converging’ and ‘diverging’ scenario at $\theta = \pi/2$ with $q_2 = 0.3$ and $K_r(0) = 2\text{eV}$ ($K_{x,y}(0) = K_r(0)/2$) for $r(0) = 0.21 r_0$ and $0.07 r_0$ ($x(0)/y(0) = -1$) are shown in Figure 5-14 for comparison with Figure 5-11 and Figure 5-13. In Figure 5-13 it was shown that $\text{dir}_{x,y}$ can have a significant effect on the trajectories in x and y separately. However, although $\text{dir}_{x,y}$ has a small effect on overall radial amplitude, the major contributing factors are $K_r(0)$ and $r(0)$, and the major consequence of changing $\text{dir}_{x,y}$ is to shift the trajectory maxima and minima. Radially, $\text{dir}_{x,y}$ has little effect on trajectory amplitude.

### 5.3.6 Initial Radial Velocity Direction vs. Initial rf Phase

Figure 5-15 is included for comparison with Figure 5-10 for $x(0) = -y(0) = 0.15 r_0$ ($r(0) = 0.21 r_0$). Shown are the 2 largest and the 2 least amplitude trajectories produced with $q_2 = 0.3$ and $K_{x,y}(0) = 1\text{eV}$ for 9 values of $\theta$ from 0 to $\pi$ calculated in steps of $\pi/8$. Again, $\text{dir}_{x,y}$ does not significantly affect the overall maximum radial amplitudes but does cause a shift in peak positions and in the phases at which maximum or minimum amplitude trajectories are produced.

Figure 5-16 shows the maximum amplitudes attained in $x$, $y$ and $r$ for $q_2 = 0.3$, $K_{x,y}(0) = 1\text{eV}$ and $x(0) = -y(0) = 0.05 r_0$ over $\text{Ln}_{rf} = 30$ and $0 \leq \theta \leq \pi$. The asymmetry of Eq 5.6 is seen in the asymmetric progression of the x and y maxima, $x(\theta+\pi) \approx y(\theta)$. Over the full range of initial phases, $\text{dir}_{x,y}$ plays little role in determining radial trajectory amplitude. ‘Converging’ trajectories over $\pi \leq \theta \leq 2\pi$ are very similar to ‘diverging’ trajectories over $0 \leq \theta \leq \pi$.

Ion motion in the x- and radial directions are compared over $0 \leq \theta \leq \pi$ under ‘converging’ and ‘diverging’ scenarios for ions with ‘thermal’ radial energy ($K_{x,y} = 0.025\text{eV}$) in Figure 5-17.
Initial ion and rf field conditions correspond to Table 5.1 and $q_2 = 0.3$; $x(0)/y(0) = -1$ for $r(0) = 0.21r_0$ and $0.07r_0$; $K_r(0) = 2eV$ ($K_{x,y}(0) = K_r(0)/2$); $\theta = \pi/2$. Plotted are the radial trajectory amplitudes for two conditions: ‘converging’ in which both $v_x(0)$ and $v_y(0)$ are directed towards the z-axis, and ‘diverging’ in which they are both directed away from the z-axis. Changing $\text{dir}_{x,y}$ mainly affects the peak positions and has a small effect on trajectory amplitudes.
Initial ion and rf field conditions correspond to Table 5.1 and $q_2 = 0.3$; $x(0)/y(0) = -1$; $r(0) = 0.21r_0$; $K_z(0) = 2\text{eV}$ ($K_{x,y}(0) = K_z(0)/2$). Plotted are radial trajectory amplitudes for two conditions: ‘converging’ in which both $v_x(0)$ and $v_y(0)$ are directed towards the z-axis, and ‘diverging’ in which they are both directed away from the z-axis. Trajectories were calculated over the range $0 \leq \theta \leq \pi$ in steps of $\pi/8$, as was done for Figure 5-10 for the ‘diverging’ scenario. The trajectories shown had the largest and least amplitudes of those calculated. Changing the initial velocity direction has the major effect of shifting peak positions and also shifting the phase at which trajectory amplitudes are maximized and minimized.
Figure 5-16: Maximum Effective Potential vs. Initial rf Phase and Initial Ion Velocity Direction

Initial ion and rf field conditions correspond to Table 5.1 and \( q_2 = 0.3; x(0)/y(0) = -1; r(0) = 0.21r_0; K_r(0) = 2eV \) \((K_{x,y}(0) = K_r(0)/2)\). Plotted is the maximum effective potential experienced by an ion versus the initial rf phase \( \theta \) (Eq 5.6) with \( Ln_{rf} = 30 \) for two conditions: ‘converging’ in which both \( v_x(0) \) and \( v_y(0) \) are directed towards the z-axis, and ‘diverging’ in which they are both directed away from the z-axis. The right axis ticks correspond to the effective potential while the labels indicate the position at which \( V^*(x, y, r) \) is attained. Since \( V^*(x,y,r) \propto (x,y,r/r_0)^2 \) the right hand scale is not linear with position.

Although \( \text{dir}_{x,y} \) can have a significant effect on trajectory amplitudes in \( x \) or \( y \) separately, radially it has little influence on overall amplitude but does shift the peak positions and the values at which \( \theta \) produces trajectories of maximum or minimum overall radial amplitudes. As before, \( \theta \) has a significant influence on both radial and \( x \) trajectory amplitudes, and there is more variation with \( \theta \) for the larger \( q_2 \) trajectories although they are confined to a smaller radius.

Two dimensional projections of these trajectories are plotted in Figure 5-18. Trajectories broaden as \( \theta \to \pi/2 \) when the initial acceleration is minimum and then narrow again as \( \theta \to \pi \) where the acceleration is maximum. Lower \( q_2 \) trajectories are narrower than the larger \( q_2 \).
counterparts but extend further towards $r_0$ radially. The effect of $\text{dir}_{x,y}$ is essentially to reflect the projections: trajectories in the ‘converging’ scenario for $\pi \leq \theta \leq 2\pi$ would be very similar to those under the ‘diverging’ scenario for $0 \leq \theta \leq \pi$ and vice versa. Over the full range of $\theta$ there would be minimal difference for an ion beam that was converging versus diverging.

Figure 5-17: Influence of Initial rf Phase and Initial Ion Velocity Direction on Ion Trajectories

![Figure showing ion trajectory projections](image)

Initial ion and rf field conditions correspond to Table 5.1 and $q_z = 0.3$ or $\sqrt{2/10}$; $x(0) = y(0) = 0.05r_0$; $K_{x,y}(0) = 0.025eV$ (‘thermal’ radial energy). Plotted are the trajectories for $x$- and radial ion motion in an ideal rf quadrupole field for several values of initial rf phase for $L_{\text{nr}} = 30$. Two initial conditions are compared: ‘converging’ (Con) in which both $v_x(0)$ and $v_y(0)$ are directed towards the $z$-axis, and ‘diverging’ (Div) in which they are both directed away from the $z$-axis. Although the initial direction of ion motion can have a significant effect on trajectory amplitudes in $x$ or $y$ separately, radially it has little influence on overall amplitude but does shift the peak positions. As before, $\theta$ has a significant influence on both radial and $x$ trajectory amplitudes, and there is more variation with $\theta$ for the larger $q_z$ trajectories although they are confined to a smaller radius. Note that the $x(t)/r_0$ and $r(t)/r_0$ axes use different scales. Figure 5-18 shows two dimensional projections.
5.3.7 General Discussion: Implications for Ion Transmission

Over the last 10 years applications have emerged that involve deceleration of large current (nA – μA), high kinetic energy (keV) ion beams for low energy (< 50 eV) injection into collision cells for isobar separation or cooling, such as the ISA. Such beams typically suffer from relatively large radial energy compared to weaker low energy beams produced, for example, by
electrospray ionization (ESI) or matrix assisted laser desorption/ionisation (MALDI) sources that have become pervasive in rf quadrupole instrument applications. Exacerbating the problem, deceleration and focussing techniques can add to the divergence of the ion beam resulting in increased radial kinetic energy. Not only does this result in greater centre of mass energy during initial ion-gas collisions, as seen above ion beams will have larger amplitude trajectories once trapped by the rf quadrupole field.

Low $q_2 \leq 0.4$ is often desired in order to minimize the effects of rf heating for ion-gas interactions. RF heating is reduced at lower values of $q_2$ for fixed $\omega$ or $V_0p$ (see Eq 4.42), and ion energy is more constant over initial rf phase, $\theta$ (see Figure 5-12 and discussion). However, ion trajectory amplitudes are greater for lower $q_2$ and if the ion beam has a large radial energy spread then some of the more energetic ions may not be trapped in the low $q_2$ rf field potential. Furthermore, apertures are used at the entrances and exits of gas collision cells in order to restrict gas flow to other sections of an instrument, restricting the range of trajectory amplitudes that will be transmitted. Although trajectories are more tightly confined as $q_2 \rightarrow 0.4$, rf heating is greater than for lower $q_2$ trajectories (Figure 5-12).

The amplitudes of larger radii trajectories were also seen to vary much more with initial rf phase, $\theta$, than for small radii trajectories (Figure 5-10), and larger discrepancy was found for larger values of $q_2$. Instruments designed to handle more compact ion beams of lower radial energy and energy spread at larger values of $q_2$ may not perform as well with more energetic beams. Applications involving ion beams with a large divergence, convergence or radial distribution place special demands on rf quadrupole instrument design.

Minimizing $r(0)$ and $K_r(0)$ were found to be important factors in minimizing trajectory amplitudes, rf heating and variations in rf heating over the full range of $\theta$, while the initial velocity direction was found to play an insignificant role. For high kinetic energy ion injection, a well constructed retarding section should minimize the angular deflection of ion beams while focusing ions as close as possible to the entrance of the rf quadrupole system.

### 5.4 Multiple rf Segments in Series

Many, if not most, rf quadrupole instruments consist of two or more rf quadrupole segments. Examples include rf quadrupole drift regions before and after a collision cell for differential pumping, or an instrument employing one cell as a cooler, another as a reactor and an intermediary ion guide for pumping. Apertures are also commonly used to restrict gas flow from
collision cells to the rest of the instrument and these can cause transmission losses if not adequately designed, especially when radial ion trajectory amplitudes are large. This section considers the effect of physical spatial offsets between cells, constant \( q_2 \) with different \( \omega \) and the presence of apertures in the absence of fringing fields.

### 5.4.1 RF Quadrupole Segments with Spatial Offsets

When \( \eta \leq 0.3 \) for rf multi-poles (Eq 4.37/39, \( \eta = q_2 \) for quadrupoles), and \( q_2 \leq 0.4 \) in some cases for rf quadrupoles, ion trajectories behave on average as adiabatic systems and the total energy, \( E_{ad} \) (Eq 4.41), is conserved within narrow limits. However, in the last section \( E_{ad} \) was found to depend on factors such as \( r(0) \), \( q_2 \) and \( \theta \), and \( E_{ad} > K_r(0) + V^*(r(0)) \) was found in many instances such as Figure 5-7, Figure 5-8 and Figure 5-9.

Neglecting fringing fields, if there were a spatial offset between two adjacent cells that had the same \( r_0 \), \( \omega \) and \( q_2 \) then an ion passing between them would experience a sudden change in acceleration and potential energy as it entered a region of stronger or weaker force. The effect would depend on factors such as position, velocity and rf phase, and diametrically opposite ions in a z-axis symmetrically distributed ion beam would experience opposite changes.

Although conserved within narrow limits in each cell, \( E_{ad} \) would not necessarily have the same value in each cell and trajectory amplitude might be significantly affected. On the other hand, if the ion were not ejected from the second cell then the basic form and period of the trajectory would not be significantly affected under these conditions. Barring any further changes, such as further cell offsets or collisions with residual gas, the new trajectory properties would remain constant. This situation is analogous to ions with different \( r(0) \) or \( \text{dir}_{x,y} \) or starting at different \( \theta \) for the same \( q_2 \) value, as discussed in section 5.3.

A simple demonstration is shown in Figure 5-19 for two ions, P and N, with \( x_p(0) = 0.1r_0 \) and \( x_n(0) = -0.1r_0 \) and a cell offset of \(-0.1r_0 \) (\(-0.65\)mm) in the x-direction at two different positions with \( q_2 = 0.3 \). Y-trajectories are unaffected since ion x-, y- and z-motion is decoupled in rf quadrupole fields. Offset positions were chosen for \( L_{n_{rf}} = 2T_{0}(\omega) = 18.674 \) (bottom) and for a position where trajectories have a peak maximum (\( L_{n_{rf}} = 20 \), top). Rather than display the trajectories with the two z-axes offset by \(-0.1r_0 \) as would be the case in a physical device, the z-axes have been aligned to illustrate the effects of the offsets. This leads to apparent discontinuous ‘jumps’ in ion position at the cell offset positions, artefacts of the z-axes translations.
Figure 5-19: Ion Trajectories with rf Quadrupole Cell Position Offsets

Initial ion and rf field conditions correspond to Table 5.1, \( q_2 = 0.3, x(0) = \pm 0.1r_0, \theta = 0, \) and \( K_{x,y}(0) = 1\text{eV} \). Plotted are the x-trajectories in an ideal rf quadrupole field for ions travelling between two cells with a spatial offset of \(-0.1r_0\) in the x direction only, at two values of Ln_{rf} corresponding to a trajectory peak (Ln_{rf} = 20, top) and \(2T_0(\omega)\) (Ln_{rf} = 18.674, bottom). Rather than plotting the curves with the z-axes of the two cells offset by \(0.1r_0\), the two z-axes were aligned and the trajectories shifted to illustrate the effective jump in potential and position. The apparent discontinuous ‘jump’ in x-position at the offsets is an artifact of the choice of coordinate systems. Also plotted in black is a trajectory for an ion travelling between two cells with no spatial offset. Trajectory amplitudes change across the offsets depending on the rf phase and ion trajectory conditions, and change oppositely for the two ions that begin on opposite sides of the z-axis.

Under the special conditions in the top panel, the cell offset places P into a larger potential well at a trajectory turning point where \( E_{\text{ap}} = U_x \) and \( a_x \) is maximum, resulting in a larger amplitude for the remainder of the trajectory. On the other hand, N is placed in a lower potential well under the same conditions and there is subsequently less energy available for
conversion into kinetic energy, resulting in a lower amplitude trajectory. The offset has increased $E_{ad}$ for P and decreased it for N.

Conversely, in the bottom panel the offset occurs during a deceleration phase of the x-trajectories where $E_{ad} = K_x + U_x$. Once again, P is placed into a region of larger potential energy but now suddenly experiences a stronger deceleration, resulting in a slight decrease in trajectory amplitude. On the other hand, N is suddenly placed into a region of lower potential energy and weaker deceleration during a deceleration phase of motion, analogous to suddenly providing N with extra kinetic energy. The resulting trajectory has larger amplitude than the original. In this case, the offset has decreased $E_{ad}$ for P and increased it for N.

In general under such symmetric conditions, an offset will increase $E_{ad}$ for one ion and decrease it for the other. The differences do not necessarily cancel as the rf potential varies with $r^2$, $x^2$ or $y^2$. If apertures were present, offsets could lead to reduced transmission. Conversely, offsets could have an amplitude damping effect for ion beams that were skewed and offset from the z-axis.

5.4.2 Varying $V_{0p}$ and $\omega$ While Maintaining Constant $q_2$

A trajectory $q_2$-value can be held constant while adjusting $V_{0p}$ and $\omega$ with $q/m$ and $r_0$ constant as long as the ratio $V_{0p}/\omega^2$ remains constant (Eq 4.19/20). Conversely, $V^*(r) \propto V_{0pq_2}$ or $V^*(r) \propto (\omega q_2)^2$ separately (Eq 4.40) so that the effective potential will change for a change in $V_{0p}$ and $\omega$ even with $q_2$ held fixed. Similarly for acceleration, $a \propto V_{0p}$ or $a \propto \omega^2 q_2$ (Eq 4.15/15, 5.6) so that any change to $V_{0p}$ or $\omega$ will change the magnitude of the acceleration. While the same number of rf periods would be required for one period of the major ion oscillation period so that $T_0(\omega)$ would remain constant, the spatial length of the period relative to a fixed instrument length would be shorter for larger $\omega$. Similarly, $L_{nf}$ would be greater for larger $\omega$.

While the overall form of an ion trajectory would remain unchanged for variation of $V_{0p}$ and $\omega$ with fixed $q_2$, the time taken for a period, the amplitude and the peak positions may be greatly affected. Unlike spatial cell offsets, diametrically opposite ions in a z-axis symmetrically distributed ion beam would experience similar changes. This raises the possibility of using $V_{0p}$ and $\omega$ to restrict ion beams to smaller radii trajectories when the additional rf heating would not be problematic (as discussed below Eq 4.42, instruments using larger $V_{0p}$ and $\omega$ are ‘hotter’).

At first glance and neglecting any fringing fields it may seem straightforward that ion beams should have larger radial distributions for lower $V_{0p}$ and $\omega$ since accelerations are lower in
magnitude and ions are less strongly confined to smaller $r(t)$. In fact, as was the case in the last section, trajectory behaviour is strongly influenced by the phases of both the trajectory and rf potential at the discontinuity. These define whether the trajectory amplitude will grow or diminish, while the magnitude of the change will be affected by the trajectory amplitude, which in turn is affected strongly by $r(0)$, $K_r(0)$ and $\theta$. That is, initial conditions at entry to the first region will influence the magnitude of the change at the discontinuity while the phases of the rf potential and trajectory at the discontinuity will influence whether a trajectory grows or diminishes in amplitude.

Figure 5-20 to Figure 5-22 compare the effects of doubling $\omega$ and quadrupling $V_{0p}$ to maintain constant $q_2 = 0.2$ at 3 values of $Ln_{rf}$ for different values of the initial rf phase, $\theta$.

In Figure 5-20, $Ln_{rf}$ was set near the mid-point of the trajectory maxima where $K_r(t) \rightarrow 0$ and $E_{ad} \rightarrow U_r(t)$. The rf and trajectory phase conditions resulted in no significant changes to the $x$-trajectory amplitudes but several of the $y$-trajectories showed a significant increase in amplitude leading to significant overall radial amplitude increases for most of the trajectories. No trajectories showed a decrease in amplitude. In this situation, ions were suddenly placed in a region of larger potential energy when most of the energy was stored as potential, and ions at larger $r(t)$ (so ‘deeper’ in the potential) had larger amplitude increases.

In Figure 5-21, $Ln_{rf}$ was chosen at the tailing edge of the trajectory maxima as $K_r(t)$ was increasing and $U_r(t)$ was decreasing. All of the $x$-trajectories underwent a slight decrease in amplitude. Several of the $y$-trajectories underwent amplitude increases and others underwent amplitude decreases. The result was a spread in overall radial trajectory amplitudes, with some trajectories undergoing a net increase and others a net decrease. Ions at larger $r(t)$ gained more potential energy.

In Figure 5-22, $Ln_{rf}$ was set at a point where $U(t)$ was approaching minimum values and $K_r(t)$ maximum values. Even though $K_{x,y}(0)$ was twice that of the values for Figure 5-20 the gains in potential energy at the discontinuity were much less than those for Figure 5-20 since ions were much closer to the z-axis. Subsequently, ions were confined to much smaller amplitude trajectories in the deeper potential well.

Figure 5-23 to Figure 5-25 compare the effects of dividing $\omega$ by 2 and $V_{0p}$ by 4 to maintain constant $q_2 = 0.2$ at the same $3 Ln_{rf}$ values used above for the same initial rf phases, $\theta$.

In Figure 5-23, $Ln_{rf}$ was set near the mid-point of the trajectory maxima where $K_r(t) \rightarrow 0$ and $E_{ad} \rightarrow U_r(t)$. As was the case in Figure 5-20, the rf and trajectory phase conditions resulted in
only slight changes to the x-trajectory amplitudes. On the other hand, there were cases of decrease, increase and no significant change in amplitude for y-trajectories, and all three cases could be observed for overall radial trajectory amplitudes. For some trajectories like \( \theta = \pi/4 \) the effect was to shift the x- and y-trajectory peaks so that although there was no major change in trajectory amplitude, radially the ion would spend more time further from the z-axis following a much more elliptical path.

In Figure 5-24, \( L_{nr} \) was chosen at the tailing edge of the trajectory maxima as \( K_r(t) \) was increasing and \( U_r(t) \) was decreasing. As for the conditions in Figure 5-21, cases of decrease, increase and no significant change in y-trajectory amplitude could be observed whereas there was a fairly uniform increase for x-trajectory amplitudes instead of the decrease observed in Figure 5-21. Interestingly however, under these conditions a sort of amplitude ‘swap’ took place in the y-direction where lower amplitude trajectories under \( \omega \) became the larger amplitude trajectories under \( \omega' \), leading to a radial swap too.

In Figure 5-25, \( L_{nr} \) was set at a point where \( U(t) \) was approaching minimum values and \( K_r(t) \) maximum values. Contrary to Figure 5-22, all trajectories increased in amplitude. Although there was a relatively small loss in potential energy at the discontinuity, the large kinetic energy of the ions allowed them to penetrate much further into the weaker average \( \omega' \) rf trapping field.

From the preceding discussion it should be apparent that in order to make use of frequency offsets for ion confinement there needs to be some control over when the ions enter the offset region. If ions enter at a disadvantageous rf potential and trajectory phase combination then trajectories may actually grow instead of decrease. Having control over the \( q_2 \) value in the first region would allow one to control the trajectory period and fine adjustment could be used to avoid unwanted phase combinations.

### 5.4.3 Apertures and 'q2 focussing'

Apertures are typically introduced into rf quadrupole systems to restrict gas flow but may also restrict ion transmission. From the preceding discussions it is clear that ion trajectories for a given \( q_2 \) value have very similar periods of motion with respect to \( \omega (T_0(\omega)) \) but may have widely varying amplitudes depending on factors such as \( q_2, K_r(0), r(0) \) and \( \theta \), and peak positions depending on initial direction of motion, \( \text{dir}_{x,y} \) (Eq 5.10). The appearance of ‘saw-toothed’ peak
Initially: $x(0) = -y(0) = 0.05r_0$; dir$_{x,y} = +1, -1$ (Eq 5.10); $K_{x,y}(0) = 0.5eV$; else as in Table 5.1. A frequency offset $\omega' = 2\omega$ while maintaining constant $q_2 = 0.2$ using $V_{0p}' = 4V_{0p}$ was imposed at $L_{nrf} = 24$. Fringing fields were neglected. Potential energy gained at the discontinuity translates into larger amplitude trajectories.
Initially: $x(0) = -y(0) = 0.05r_0$; dir$_{x,y} = +1, -1$ (Eq 5.10); $K_{x,y}(0) = 1\text{eV}$; else as in Table 5.1. A frequency offset $\omega' = 2\omega$ while maintaining constant $q_2 = 0.2$ using $V_0' = 4V_0$ was imposed at Ln$_{rf} = 25.5$. Fringing fields were neglected. Gains in potential energy at the discontinuity are not sufficient to lead to larger amplitude trajectories in the deeper potential for some ions.
Initially: $x(0) = -y(0) = 0.15r_0$; dir$_{x,y} = +1, -1$ (Eq 5.10); $K_{x,y}(0) = 1eV$; else as in Table 5.1. A frequency offset $\omega' = 2\omega$ while maintaining constant $q_2 = 0.2$ using $V_0' = 4V_0$ was imposed at $Ln_{rf} = 27$. Fringing fields were neglected. There is a relatively small gain in potential energy at the discontinuity as ions are close to the z-axis and kinetic energy is approaching a maximum, and the deeper $\omega'$ potential confines ions to much smaller radii.
Initially: $x(0) = -y(0) = 0.05r_0$; dir$_{x,y} = +1,-1$ (Eq 5.10); $K_{x,y}(0) = 0.5$eV; else as in Table 5.1. A frequency offset $\omega' = \omega/2$ while maintaining constant $q_2 = 0.2$ using $V_{0p}' = V_{0p}/4$ was imposed at $Ln_{rf} = 24$. Fringing fields were neglected. Some ions experienced a sufficient loss in potential energy at the discontinuity where $E_{ad}$ is mostly in the form of potential energy so that trajectory amplitudes decreased in the shallower $\omega'$ potential well.
Initially: $x(0) = -y(0) = 0.15r_0$; $\text{dir}_{x,y} = +1, -1$ (Eq 5.10); $K_{x,y}(0) = 1 \text{eV}$; else as in Table 5.1. A frequency offset $\omega' = \omega/2$ while maintaining constant $q_2 = 0.2$ using $V_{0p}' = V_{0p}/4$ was imposed at $L_{nrf} = 25.5$. Fringing fields were neglected. Under these conditions there is an ‘amplitude swap’ in the $y$-direction as smaller amplitude trajectories under $\omega$ become larger amplitude trajectories under $\omega'$. The loss in potential energy at the discontinuity is enough to result in smaller amplitude trajectories for some ions.
Initially: $x(0) = -y(0) = 0.05r_0$; $\text{dir}_x, y = +1, -1$ (Eq 5.10); $K_{x,y}(0) = 0.025\text{eV}$; else as in Table 5.1. A frequency offset $\omega' = \omega/2$ while maintaining constant $q_2 = 0.2$ using $V_{op}' = V_{op}/4$ was imposed at $L_{nrf} = 27$. Fringing fields were neglected. There is relatively little potential energy loss at the discontinuity where ion kinetic energy is approaching a maximum and ions are able to penetrate much deeper into the shallower $\omega'$ potential.
structures during q2 scans when apertures are present has been studied previously and was seen during measurements with the ISA (discussed in chapter 8). Obviously, when trajectory amplitudes approach and exceed aperture radii then ions may be lost.

On the other hand, ions may be ‘q2-focused’ onto an aperture by scanning q2 to adjust the ion trajectory period with respect to ω (eg Eq 5.13 and 5.14) so that ions are closest to the z-axis at the aperture for a given Lnrf (Eq 4.28). Since Lnrf is different for ions with different Kz, a large energy spread in Kz can limit the effectiveness of ‘q2 focussing’; for a given q2 value some ions may be ‘focussed’ onto the aperture while others may be at a trajectory amplitude maximum or minimum. Some relevant references follow.

Alexander et al. (1989) used a 20 keV Cs+ sputter source to generate ions for injection into an rf quadrupole instrument floated at high voltage for injection energies of Kz = 50, 200 and 400 eV (figs 1-3 respectively). They adjusted V0p and were restricted to q2 < 0.16 while using m/q = 912 ions (quoted as Cs4I3+). Data were taken with Ar gas in the cell for CID work at an unspecified pressure but at levels that caused 50% attenuation of the vacuum current. A saw-toothed peak structure was observed and the maxima were attributed to $\omega k Lnrf$ $\approx$ $\omega k Lnrf$ (k an integer, Eq 5.13, Eq 4.28 in this thesis; their equation 2 appears to have a typo).

For their constant m/q = 912 scans, $\frac{Lnrf(K_z)}{Lnrf(K'_z)} = \sqrt{\frac{K'_z}{K_z}}$. As further support of their conclusion it is interesting to note that, despite the presence of Ar gas, the number of peaks observed at successive energies scales reasonably well with Kz assuming that the number of peaks is proportional to Lnrf. At Kz = 50 eV there are 5.5 peaks, Kz = 200 eV there are > 2 but < 2.5 peaks and Kz = 400 eV there is 1.5 peak: $\sqrt{50/200} \cdot 5.5 \approx 2.75$ and $\sqrt{400/200} \cdot 1.5 \approx 2.1$.

Muntean (1995) and Muntean et al. (1995) used the matrix method described in section 5.1 to produce computer calculations showing the saw-toothed peak structure in simulated q2 scans with apertures. Transmission maxima were shown to correspond strongly with values of q2 that lead to trajectories being confined closer to the z-axis at the exit aperture. Greater transmission losses at small and large q2 were also shown to accompany beams with greater divergence and larger r(0). This can be understood from section 5.3 as greater r(0) leads to larger amplitude trajectories, and trajectory amplitudes are greatest for the lowest and largest stable q2 trajectories (for example, see Figure 5-1, Figure 5-2, Figure 5-8 and Figure 5-9).
Blaum et al. (2000) were also able to produce computer calculations that gave the form of experimentally observed saw-toothed peak structures, further illustrating the importance of tuning \(q_2\) to match \(T_0(\omega)\) with \(L_{n_{rf}}\) and aperture dimensions.

### 5.4.3.1 Calculation Procedure and Initial Conditions

All calculations used the values from Table 5.1 and procedures from section 5.2. An initial radial kinetic energy was set with \(K_{x}(0) = K_{y}(0)\). Initial ion position was then rotated about a ring of radius \(r(0) = 0.05r_0\) or \(0.15r_0\) (0.325, 0.975mm) with \(x(0) = r(0)\cos \phi\) and \(y(0) = r(0)\sin \phi\) for either 36 or 37 evenly spaced steps of \(\Delta \phi\) and \(0 \leq \phi < 2\pi\). Velocities were always directed away from the z-axis for a ‘diverging beam’ scenario. At each position, trajectories were calculated for either 12 or 13 different initial phases, \(0 < \theta < 2\pi\), with \(\Delta \theta\) evenly spaced. The process was repeated for \(0 < q_2 < 1\) with \(\Delta q_2 = 0.01\) so that at each \(q_2\) value either 432 (36x12) or 481 (37x13) trajectories were analyzed, and a total of 43632 or 48581 trajectories were analyzed for each full \(q_2\) range scan. Fringing field effects were neglected.

Two criteria were evaluated: a) whether or not a given trajectory remained confined to the quadrupole limit \(r_0\); and b) whether or not an ion with such a trajectory could pass 1, 2 or 3 apertures in series. If at any point criterion Eq 5.12 was met so that \(r(t) > r_0\) then the ion was considered ejected from the system and calculation stopped. Any apertures not yet encountered were considered as not passed.

Apertures were defined by a value of \(L_{n_{rf}}\) (30, 37, 45, 60) and a radius, \(r_{ap} = 0.15r_0\) or 0.23\(r_0\) (0.975, 1.495mm). If \(r(L_{n_{rf}}) < r_{ap}\) then the ion was considered to have passed the aperture. Even if an ion did not pass an aperture, calculation continued until either \(r(t) > r_0\) (criterion Eq 5.12 was met) or \(L_{n_{rf}}\) of the final aperture was exceeded. The programme recorded which apertures were passed and, in cases where ions were ejected from the system, the number of aperture positions passed before criterion Eq 5.12 was met.

### 5.4.3.2 Transmission through Apertures and ‘\(q_2\) Focussing’

Figure 5-26 compares transmission versus \(q_2\) over \(L_{n_{rf}} = 30\) with and without an aperture present at the end for 4 values of \(K_{x,y}(0)\) and two \(r_{ap}\). Although trajectories are theoretically stable in stability region 1 for \(0 \leq q_2 < 0.908\) (section 4.1.1), \(q_2 > 0\) is required for transmission over \(L_{n_{rf}} = 30\) because \(K_{x,y}(0)\) is sufficiently large. The onset of 100% transmission is at larger \(q_2\) for larger \(K_{x,y}(0)\) as a larger potential is required for ion confinement. As expected, there is a sharp drop to 0% transmission as \(q_2\) approaches 0.91.
Initial conditions and calculation procedures are given in section 5.4.3.1. Compared is transmission versus $q_2$ with and without an aperture present at $L_{n_{tr}} = 30$ for 4 initial radial kinetic energies, $K_{x,y}(0)$ and two aperture radii, $r_{ap}$. At low energy transmission for 2 values of $r(0)$ is also compared. The black curves show transmission without an aperture using $r(0) = 0.15 r_0 \sim 1$ mm. Although trajectories are theoretically stable in stability region 1 for $0 < q_2 < 0.908$ (section 4.1.1), $q_2 > 0$ is required for transmission over $L_{n_{tr}} = 30$ because of $K_{x,y}(0)$. The onset of 100% transmission requires larger $q_2$ for larger $K_{x,y}(0)$. Introduction of the aperture causes transmission losses that increase for smaller $r_{ap}$ and for larger $r(0)$, $K_{x,y}(0)$ and extreme values of $q_2$ where trajectory amplitudes are greatest.

Introduction of an aperture causes transmission losses in all cases. Many of the curves are ‘jagged’, showing sharp rises and drops in transmission with changes in $q_2$ due to the ‘$q_2$ focusing’ discussed in the introduction of section 5.4.3. Trajectory periods are affected by $q_2$ and transmission maxima represent $q_2$ values that result in trajectories being, on average, closer to the $z$-axis at the aperture and vice versa. Such effects are more pronounced for conditions
promoting larger amplitude trajectories (larger $K_{x,y}(0)$ and $r(0)$, and extreme values of $q_2$), and for smaller $r_{ap}$ representing more restrictive apertures.

A $z$-translational energy spread, $\Delta K_z$, would result in a spread in the physical positions of the trajectory maxima and minima, although the positions relative to the number of rf-cycles ($T_0(\omega)$) would be the same. Generally, this would result in increased transmission at the transmission minima of Figure 5-26 and decreased transmission at the maxima, with the magnitude depending on the extent and distribution of the energy spread. Also, in a typical ion beam ions are restricted neither to a single ring $r(0)$ nor to a single value of radial kinetic energy $K_{x,y}(0)$. Addition of these factors into the calculations is straightforward and should result in smoother transmission curves, but is beyond the scope of the present work.

The issue is taken up further in Figure 5-27 and Figure 5-28 for transmission through a single aperture located at either $L_{n_{rf}} = 30, 45$ or $60$ for $0 \leq q_2 \leq 0.4$ for $K_{x,y}(0) = 1$ and $0.5$ eV as these did not have flat-top transmission over the $q_2$ range. A smaller step, $\Delta q_2 = 0.002$, was used as $\Delta q_2 = 0.01$ was found to be too coarse to see some peaks. Transmission maxima are expected when $L_{n_{rf}} = k/2 \cdot T_0(\omega)$, $k$ an integer. Approximately then at low $q_2$ (Eq 5.13),

\[
q_2 = \frac{\sqrt{2} \cdot k}{L_{n_{rf}}}
\]

should result in transmission maxima but may be offset slightly by factors such as initial rf phase and ion velocity direction as discussed in section 5.3. Expected ‘$q_2$ focus values’ for transmission maxima are tabulated in Table 5.5.

<table>
<thead>
<tr>
<th>Number of Periods (k/2)</th>
<th>$L_{n_{rf}} = 30$</th>
<th>$L_{n_{rf}} = 45$</th>
<th>$L_{n_{rf}} = 60$</th>
<th>Number of Periods (k/2)</th>
<th>$L_{n_{rf}} = 30$</th>
<th>$L_{n_{rf}} = 45$</th>
<th>$L_{n_{rf}} = 60$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>4.5</td>
<td>0.424</td>
<td>0.283</td>
<td>0.212</td>
</tr>
<tr>
<td>0.5</td>
<td>0.047</td>
<td>0.031</td>
<td>0.024</td>
<td>5</td>
<td>0.471</td>
<td>0.314</td>
<td>0.236</td>
</tr>
<tr>
<td>1</td>
<td>0.094</td>
<td>0.063</td>
<td>0.047</td>
<td>5.5</td>
<td>0.519</td>
<td>0.346</td>
<td>0.259</td>
</tr>
<tr>
<td>1.5</td>
<td>0.141</td>
<td>0.094</td>
<td>0.071</td>
<td>6</td>
<td>0.566</td>
<td>0.377</td>
<td>0.283</td>
</tr>
<tr>
<td>2</td>
<td>0.189</td>
<td>0.126</td>
<td>0.094</td>
<td>6.5</td>
<td>0.613</td>
<td>0.409</td>
<td>0.306</td>
</tr>
<tr>
<td>2.5</td>
<td>0.236</td>
<td>0.157</td>
<td>0.118</td>
<td>7</td>
<td>0.660</td>
<td>0.440</td>
<td>0.330</td>
</tr>
<tr>
<td>3</td>
<td>0.283</td>
<td>0.189</td>
<td>0.141</td>
<td>7.5</td>
<td>0.707</td>
<td>0.471</td>
<td>0.354</td>
</tr>
<tr>
<td>3.5</td>
<td>0.330</td>
<td>0.220</td>
<td>0.165</td>
<td>8</td>
<td>0.754</td>
<td>0.503</td>
<td>0.377</td>
</tr>
</tbody>
</table>

Transmission maxima in the figures are in excellent agreement with Eq 5.15 and Table 5.5, clearly illustrating ‘$q_2$ focusing’. Furthermore, the larger $K_{x,y}(0)$ trajectories of Figure 5-27...
had larger amplitudes and, as discussed in section 5.3, trajectory amplitudes also increase as \( q_2 \) decreases below a threshold value (e.g. seen from 0.25 to 0.1 in Figure 5-1). Accordingly, transmission peaks begin at lower \( q_2 \) in the lower \( K_{x,y}(0) \) transmission calculations, and there is better transmission as \( q_2 \) increases from 0.24 to 0.4.

From Eq 5.15 it is apparent that under conditions \( \alpha \) and \( \beta \) such that \( \ln_{\text{rf}}^\alpha = \mu \ln_{\text{rf}}^\beta \) with other conditions identical and \( \mu \) a real number (for example, cell \( \alpha \) is twice the physical length of cell \( \beta \)), there can be more ‘\( q_2 \) focus values’ under \( \alpha \) than under \( \beta \) over the same \( q_2 \) interval. For example, an ion that arrives at \( \ln_{\text{rf}} = 30 \) at \( 1.75T_0(\omega) \) will arrive at \( \ln_{\text{rf}} = 60 \) at \( 3.5T_0(\omega) \). This can also be seen in Table 5.5: over the range \( 0 < q_2 < 0.38 \) there are 15 ‘\( q_2 \) focus values’ for \( \ln_{\text{rf}} = 60 \), 11 for \( \ln_{\text{rf}} = 45 \) and only 7 for \( \ln_{\text{rf}} = 30 \).

This is also illustrated in Figure 5-27 and Figure 5-28 where it is seen that \( \ln_{\text{rf}} = 60 \) yields the most transmission peaks, followed by \( \ln_{\text{rf}} = 45 \) and 30 respectively. In Figure 5-28, transmission with no aperture begins for \( 0.5 < \ln_{\text{rf}}/T_0(\omega) < 0.75 \) for the \( \ln_{\text{rf}} = 30 \) panel. Transmission with aperture 1 begins for \( \ln_{\text{rf}}/T_0(\omega) = 1 \). On the other hand, these values correspond to the onset of transmission at \( 1 < \ln_{\text{rf}}/T_0(\omega) < 1.5 \) for the \( \ln_{\text{rf}} = 60 \) panel and transmission with aperture 3 begins for \( \ln_{\text{rf}}/T_0(\omega) = 1.5 \), representing an extra peak compared to the \( \ln_{\text{rf}} = 30 \) aperture position. Peaks are closer together in \( q_2 \) value for larger \( \ln_{\text{rf}} \) because there is a higher density in \( q_2 \) values for which ions arrive at the aperture at integral and half-integral points in the trajectory period.

Practically, the density of peaks is limited by the attainable \( \ln_{\text{rf}} \) of the system and these simple calculations do not account for other losses due to scattering from collision or residual gases present in a cell. However, they do point to some advantages of larger \( \ln_{\text{rf}} \), for example by using longer rf quadrupole cells. For instance, in applications where larger amplitude ion beams must be focused through apertures then tuning may be easier, and if the number of rf voltage supplies is limited and cells must share one supply then better transmission may be possible.

Figure 5-29 and Figure 5-30 illustrate the effect of adding more than 1 aperture to the system. Combinations of 2 and 3 apertures were studied with \( r_{\text{ap}} = 0.15r_0 \) or \( 0.23r_0 \) at positions of either \( \ln_{\text{rf}} = 30, 37, 45, 57 \) or 60 for \( r(0) = 0.05r_0 \) and \( K_{x,y}(0) = 0.5 \) eV. The value of \( q_2 \) was not varied between each aperture to attempt ‘\( q_2 \) focusing’ from one aperture to the next, but the aperture positions were chosen so that at times the various \( \ln_{\text{rf}} \) had common factors (30 = 2x15, 45 = 3x15, 60 = 4x15 = 2x30) and at others they did not (37 and 57 are prime numbers).
Figure 5-27: ‘q2 Focusing’ for Kx,y(0) = 1 eV and 1 Aperture

Initial conditions and calculation procedures are given in section 5.4.3.1 except that a finer Δq2 = 0.002 step was used; r(0) = 0.05r0 ~ 0.3 mm and Kx,y(0) = 1 eV. Transmission through 1 aperture of radius r_ap = 0.23r0 ~ 1.5 mm versus q2 is compared for 3 different aperture positions, 1, 2 and 3 at Lnrf = 30, 45 and 60 respectively.

The top panels show the transmission results for each aperture position individually (black, red or blue) compared to the results with no aperture present (purple with varying line patterns). The top axis shows the calculation q2 value. The bottom axis shows the expected fraction of trajectory periods completed by the positions (Lnrf) of the apertures as calculated using Eq 5.15 (eg. bottom axis shows k/2). The bottom panel compares the transmission results for the three different positions using the solid line colour and ‘no aperture’ line patterns of the top panels. Note the top and bottom panels have the top and bottom axes reversed.

Transmission peaks correspond well with the expected q2 values corresponding to completion of integral or half-integral periods over a given Lnrf from Eq 5.15 and Table 5.5. As expected, the approximation gets worse as q2 → 0.4 (see Eq 5.13 and Table 5.4). Shifts in peak values are also expected from factors such as r(0) and initial velocity direction.
Initial conditions and calculation procedures are given in section 5.4.3.1 except that a finer $\Delta q_2 = 0.002$ step was used; $r(0) = 0.05r_0 - 0.3$ mm and $K_{x,y}(0) = 0.5$ eV. Transmission through 1 aperture of radius $r_{ap} = 0.23r_0 - 1.5$ mm versus $q_2$ is compared for 3 different aperture positions, 1, 2 and 3 at $Ln_{rf} = 30, 45$ and 60 respectively.

The top panels show the transmission results for each aperture position individually (black, red or blue) compared to the results with no aperture present (purple with varying line patterns). The top axis shows the calculation $q_2$ value. The bottom axis shows the expected fraction of trajectory periods completed by the positions ($Ln_{th}$) of the apertures as calculated using Eq 5.15 (eg. bottom axis shows $k/2$). The bottom panel compares the transmission results for the three different positions using the solid line colour and ‘no aperture’ line patterns of the top panels. Note the top and bottom panels have the top and bottom axes reversed.

Transmission peaks correspond well with the expected $q_2$ values corresponding to completion of integral or half-integral periods over a given $Ln_{rf}$ from Eq 5.15 and Table 5.5. As expected, the approximation gets worse as $q_2 \to 0.4$ (see Eq 5.13 and Table 5.4). Shifts in peak values are also expected from factors such as $r(0)$ and initial velocity direction.
In Figure 5-26 it was shown that, under all conditions studied, the addition of an aperture caused transmission losses, and in many cases there was no flat-top transmission with an aperture present. In Figure 5-29 it is seen that, in cases where flat-topped transmission is present with 1 aperture ($r_{ap} = 0.23r_0$ only for $K_{x,y}(0) = 0.5$ eV), addition of a second aperture does not significantly reduce the $q_2$ range for flat-top transmission, regardless of the position of the aperture. It does, however, reduce the number of transmission peaks in regions where flat-topped transmission is not achieved with 1 aperture, and more restrictive apertures cause greater losses.

When flat-topped transmission is achieved, trajectory amplitudes are on average already approaching or smaller than $r_{ap}$ over the range of $q_2$ so that additional apertures of the same or larger $r_{ap}$ should not significantly affect the transmission. On the other hand, in regions where transmission is heavily dependent on ‘$q_2$ focusing’ so that transmission is not flat-topped, it is not surprising that addition of more apertures causes further losses. In Figure 5-29, losses were minimized when the second aperture was at $2L_{n rf}$ the first aperture ($L_{n rf} = 30$ and 60).

Addition of a third aperture is studied in Figure 5-30, with the first column graphs included for comparison with 2-aperture transmission. Again, transmission in regions of flat-topped transmission with 1 or 2 apertures was not significantly affected by addition of a third aperture of equal $r_{ap}$ since trajectory amplitudes were already approaching or smaller than $r_{ap}$ on average. However, the additional peaks in non-flat-topped transmission regions were significantly reduced, as expected, since they are more dependent on the $L_{n rf}$ and $q_2$ combination according to Eq 5.15. Addition of a third aperture had a much greater affect on this than a second, and it would be expected that addition of a fourth aperture would again greatly diminish the number of non-flat-topped transmission peaks. This could be useful for reducing peak structure during m/q scans in some cases. Interestingly, although the peaks are more evenly spaced when apertures are placed at $L_{n rf} = 30, 45$ and 60, there is no significant difference in the number of 100% transmission peaks as when the $L_{n rf}$ positions of the three apertures have no common factors.

5.4.3.3 Conclusions

Better transmission through apertures without use of focussing fields is achieved at lower radial kinetic energy, $K_{x,y}(0)$ where trajectory amplitudes are smaller. When larger trajectory beams are to be transmitted, larger apertures can aid in increasing transmission and gas cooling can be used to reduce trajectory amplitudes. Using longer collision cells can have several
benefits. First, a larger density of ‘q₂ focus values’ provides more tuning options and could alleviate some problems if multiple rf quadrupole regions are to be controlled by the same rf voltage supply. Secondly, for collision cells, lower gas pressures can be used with the benefit of allowing wider apertures for gas flow restriction while maintaining the same average number of collisions per ion inside the cell.

When transmission is not flat-topped, control of q₂ between apertures would allow one to use ‘q₂ focusing’ to increase transmission. If q₂ control were not possible then tuning for consistently high transmission on a daily basis would likely be very difficult and time-consuming. However, if ion trajectories are on average less than aperture radii then obviously the placement of apertures makes little difference. For large radial energy ion beams, an initial, long cooling cell with wide apertures and good control of q₂ between different rf quadrupole segments could provide many advantages for transmission through a subsequent reaction cell.
Initial conditions and calculation procedures are given in section 5.4.3.1 with $K_{x,z}(0) = 0.5 \text{ eV}$, $r(0) = 0.05r_0$ ($0.0325 \text{ mm}$) and aperture radii $r_{ap} = 0.15r_0$ or $0.23r_0$ ($0.975$ or $1.495 \text{ mm}$). Transmission through 2 apertures of equal $r_{ap}$ versus $q_2$ is shown. The column heading gives the position of the apertures in terms of $L_{n_{rt}}$ in the order passed, and the $r_{ap}$ of the aperture is shown along the right-hand side of each row. Flat-topped transmission is achieved with 2 apertures in regions where it is achieved with only 1 aperture, and very nearly extends over the same range of $q_2$ (see Figure 5-26) regardless of the position of the second aperture. Flat-topped transmission is not achieved using the smaller $r_{ap}$ apertures. In regions with no flat-topped transmission, where 'q2 focusing' has a strong influence on transmission, the number of peaks is reduced with addition of a second aperture. Use of the second aperture at $2L_{n_{rt}}$ of the first ($L_{n_{rt}} = 30$ and $60$) reduces the losses.
Initial conditions and calculation procedures are given in section 5.4.3.1 with $K_{x+y}(0) = 0.5$ eV, $\tau(0) = 0.05r_0$ ($\sim 0.0325$ mm) and aperture radii $r_{ap} = 0.15r_0$ or $0.23r_0$ (0.975 or 1.495 mm). Transmission through 3 apertures of equal $r_{ap}$ versus $q_2$ is shown in columns 2 – 4. Transmission through 2 apertures is shown in column 1, reproduced from column 2 of Figure 5-29, for comparison. The column heading gives the position of the apertures in terms of $L_{n_{rf}}$ in the order passed, and the $r_{ap}$ of the aperture is shown along the right-hand side of each row.

Flat-topped transmission is achieved with 3 apertures in regions where it is achieved with 1 or 2 aperture(s), and very nearly extends over the same range of $q_2$ (see Figure 5-26) regardless of the position of the second aperture. Flat-topped transmission is not achieved using the smaller $r_{ap}$ apertures. In regions with no flat-topped transmission, where ‘$q_2$ focusing’ has a strong influence on transmission, the number of peaks is significantly reduced with addition of a third aperture. Use of apertures at $L_{n_{rf}} = 30, 45$ and 60 results in a more even spacing of transmission peaks, however does not result in significantly more peaks of 100% transmission than when the apertures are placed at positions with no common factors.
6 Ion-Gas Interactions

Unwanted electron detachment can be a major concern for anion-neutral interactions in rf quadrupole collision cells given the relatively weak electron binding of many anions. While this has been addressed for anion cooling (Liu et al. 2007), unwanted reactions, electron transfers and cluster formations can also pose a significant source of anion loss.

Some basic concepts needed to understand the reaction energy available during a reaction, sources of barriers and an elementary first-order estimate calculation for evaluating collision gases are developed for use in the following chapters and as a general reference. This section is by no means meant to be comprehensive, but rather to cover some very elementary concepts that are useful in understanding ion-gas interactions in the meV to several eV range of kinetic energy.

6.1 Kinetic Energy Transfer and Conversion

A basic exercise in introductory physics courses is to derive equations describing the kinetic energy transferred during elastic collisions between two ‘hard spheres’ using conservation of energy and momentum, such that no energy is lost to phenomena such as deformation or heating. Long range forces, such as screened coulomb scattering, will not be considered in this section but are discussed later in the chapter.

A very elementary but illustrative situation is non-relativistic, 1-dimensional (1-D, \( \theta = 0 \) or \( \pi \) in Figure 6-1, often referred to as ‘head-on’) purely elastic (kinetic energy is not converted to other forms such as internal energy of a particle) 2-particle scattering by central conservative forces. With mass \( m \), laboratory (lab) frame velocity magnitude \( v \), momentum \( p = mv \), kinetic energy \( K = p^2/2m \), prime superscript (\( v' \)) denoting “after the collision” and un-primed (\( v \)) denoting “initial” (“initial” and “after” refer to large enough separations that any long-range interaction effect is sufficiently small to be ignored):

\[
\text{Eq 6.1 \ conservation of } p: \quad m_1v_1 + m_2v_2 = m_1v'_1 + m_2v'_2 \\
\Rightarrow m_1(v_1 - v'_1) = -m_2(v_2 - v'_2)
\]

\[
\text{Eq 6.2 \ conservation of } K: \quad \frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2 = \frac{1}{2}m_1v'_1^2 + \frac{1}{2}m_2v'_2^2 \\
\Rightarrow m_1(v_1 - v'_1)(v_1 + v'_1) = -m_2(v_2 - v'_2)(v_2 + v'_2)
\]
Figure 6-1: Laboratory and Centre of Mass Frames of Reference

A non-relativistic energy ‘collision’ between 2 particles of masses $m_1$ and $m_2$, $m_2$ initially at rest, is depicted with prime superscripts ($v'$) representing ‘after the collision’ and un-primed ($v$) ‘before’ (“before” and “after” refer to large enough separations that any long-range interaction effect is sufficiently small to be ignored). Laboratory (lab) frame velocities are denoted by $v$ and centre of mass frame velocities by $u$. In a) $v_2 = 0$ since $m_2$ is initially at rest in the lab frame. After the collision, $m_1$ travels at a reduced speed at an angle $\theta$ relative to the initial velocity direction (aligned with the x-axis) and $m_2$ at an increased speed ($v'_2 \neq 0$) at an angle $\alpha$ with the x-axis. The so called impact parameter, $b$, which represents the closest approach of $m_1$ and $m_2$ ‘before’ the collision, is also shown. If $b < r_1 + r_2$ (the radii of $m_1$ and $m_2$) then there is always a collision between neutrals with no long-range forces. For $m_1 < m_2$, $\theta < \pi/2$. In b) a similar collision is depicted. While $v_2 = 0$, after coordinate transformation to the CM frame. In an elastic collision $u = u'$ for both $m_1$ and $m_2$, and both scatter at the same angle $\phi$ relative to the x-axis (aligned with $v_1$) as shown. From conservation of momentum, the angle $u_1u_2$ and $u'_1u'_2$ is always $\pi$. The fundamental nature of elastic collisions is much clearer in the CM frame.

Division of Eq 6.2 by 6.1 shows that the magnitude of the relative velocity of the two particles remains constant,

**Eq 6.3**

$$v_{rel} = v_1 - v_2 = v'_2 - v'_1$$

If one of the particles were initially at rest (eg. $v_2 \approx 0$) then kinetic energy, however little (see Table 6.2), would necessarily be transferred from the one in motion to the other. This is the basic mechanism of cooling. As will be discussed below Eq 6.28, non-elastic collisions may have advantages in some situations.

Solving for $v'_1$ and $v'_2$ yields the following:
Table 6.1: Two-Particle Head-on Elastic Collision

<table>
<thead>
<tr>
<th>general</th>
<th>$v'_1 = \left(\frac{m_1 - m_2}{m_1 + m_2}\right) v_1 + \left(\frac{2m_2}{m_1 + m_2}\right) v_2$</th>
<th>$v'_2 = \left(\frac{2m_1}{m_1 + m_2}\right) v_1 + \left(\frac{m_2 - m_1}{m_1 + m_2}\right) v_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_1 = m_2$</td>
<td>$v'_1 = v_2$</td>
<td>$v'_2 = v_1$</td>
</tr>
<tr>
<td>$m_1 \gg m_2$</td>
<td>$v'_1 \approx v_1$</td>
<td>$v'_2 \approx 2v_1 + v_2$</td>
</tr>
<tr>
<td>$m_2 \gg m_1$</td>
<td>$v'_1 \approx 2v_2 - v_1$</td>
<td>$v'_2 \approx v_1$</td>
</tr>
</tbody>
</table>

Solutions to Eq 6.1 and 6.2, $m$ mass, $v$ velocity (lab frame); superscript, “′” = “after the collision”, un-superscripted represents initial velocity.

Initial cooling or reacting with the ISA currently involves relatively high kinetic energy anions ($5 – 10$ eV) incident on thermal ($0.025$ eV) gas molecules/atoms. Let $m_1$ be the anion, $m_2$ the ‘target’ gas molecule/atom and $K_0$ be the initial kinetic energy. Then $v_2 \sim 0$ so that $K_0 = K_1$. Table 6.2 summarizes some general results.

Table 6.2: Two-Particle Head-on Elastic Collision with one Particle Initially at Rest

<table>
<thead>
<tr>
<th>case</th>
<th>general</th>
<th>$v'_1 = \left(\frac{m_1 - m_2}{m_1 + m_2}\right) v_1$</th>
<th>$\Delta K_1 = \frac{4m_1 m_2}{(m_1 + m_2)^2} K_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>case I</td>
<td>$m_1 = m_2$</td>
<td>$v'_1 = 0$</td>
<td>$\Delta K_1 = K_0$</td>
</tr>
<tr>
<td>case II</td>
<td>$m_1 &gt; m_2$</td>
<td>$v'_1 &gt; 0$</td>
<td>$\Delta K_1 &lt; K_0$</td>
</tr>
<tr>
<td>case III</td>
<td>$m_2 &gt; m_1$</td>
<td>$v'_1 &lt; 0$</td>
<td>$\Delta K_1 &lt; K_0$</td>
</tr>
<tr>
<td>case IV</td>
<td>$m_1 &gt;&gt; m_2$</td>
<td>$v'_1 \approx v_1$</td>
<td>$\Delta K_1 \approx 0$</td>
</tr>
<tr>
<td>case V</td>
<td>$m_2 &gt;&gt; m_1$</td>
<td>$v'_1 \approx -v_1$</td>
<td>$\Delta K_1 \approx 0$</td>
</tr>
</tbody>
</table>

Solutions to Eq 6.1 and 6.2, $m$ mass, $v$ velocity (lab frame); superscript, “′” = “after the collision”, un-superscripted represents initial velocity. Since $v_2 = 0$, the initial kinetic energy is $K_0 = K_1$. The change in kinetic energy for $m_1$ is $\Delta K_1 = K_0 - K'_1$. See Table 6.1 for $v_2 \neq 0$.

To see cases III and IV and confirm conservation of energy, express $m_1 = a \cdot m_2$ with $a \in \mathbb{R}(0, \infty)$; then $\Delta K_1 = \frac{4 \cdot a}{(a+1)^2} K_0$. If $\Delta K_1 > K_0 \Rightarrow 4a > (a+1)^2 \Rightarrow 0 > (a-1)^2$, which is not possible for real numbers. Only when the two masses are equal, $a = 1$, does $\Delta K_1 = K_0$, the maximum kinetic energy loss for these 1-D elastic collisions.
While this model is obviously very simplistic, several observations are generally useful. Some mechanism would be needed to maintain forward motion for cases II and IV since the ion loses all kinetic energy in case II and travels backwards for case IV. The contrary is true for case III. This is one advantage of using a cooling gas consisting of atoms/molecules less massive than the incident ions. Of course, as shown in case V, to achieve the same amount of cooling with a cooling gas consisting of less massive atoms/molecules as one with more massive constituents requires more collisions on average (e.g. higher pressure or a longer ion-gas interaction region).

Following the same procedure as just outlined, 2-dimensional (2-D) non-relativistic elastic collisions can be examined in the lab frame, as depicted in Figure 6-1. Also shown is the impact parameter, b. Generally, for large b there is little or no scattering while b = 0 represents a head-on collision so that scattering angle, \( \theta \), is generally a decreasing function of b. Derivation of the relationship between b and \( \theta \) requires knowledge of the interaction potential.

For the following, \( v_2 = 0 \) will be assumed since this reasonably approximates initial cooling and reaction conditions in the ISA and many other experiments. Conservation of kinetic energy, \( K \), and momentum, \( p \), can be expressed by:

\[
\text{Eq 6.4} \quad \text{conservation of } p_x: \quad m_1 v_1 = m_1 v'_1 \cos \theta + m_2 v'_2 \cos \alpha \\
\Rightarrow m_1^2 v_1^2 = 2m_1^2 v_1 v'_1 \cos \theta + m_1^2 v'_1^2 \cos^2 \theta + m_2^2 v'_2^2 \cos^2 \alpha
\]

\[
\text{Eq 6.5} \quad \text{conservation of } p_y: \quad 0 = m_1 v'_1 \sin \theta - m_2 v'_2 \sin \alpha \\
\Rightarrow m_1^2 v'_1^2 \sin^2 \theta = m_2^2 v'_2^2 \sin^2 \alpha
\]

\[
\text{Eq 6.6} \quad \text{conservation of } K: \quad m_1 v_1^2 = m_1 v'_1^2 + m_2 v'_2^2
\]

In the special case that \( m_1 = m_2 = m \), mass can be divided out of Eq 6.4 – 6.6 leaving only velocity magnitudes and angles. From Eq 6.6 it is seen that the velocity vectors form a right angle triangle with hypotenuse \( v_1 \): for such elastic collisions between 2 equal masses, the final velocities of the 2 particles are at right angles to one-another. Adding the second (squared) forms of Eq 6.4 and 6.5, and substitution using Eq 6.6 arranged for \( v'_2^2 \) yields the following:

\[
\text{Eq 6.7} \quad v'_1 = v_1 \cos \theta \\
\text{Eq 6.8} \quad K'_1 = K_1 \cos^2 \theta \\
\text{Eq 6.9} \quad v'_2 = v_1 \sin \theta \\
\text{Eq 6.10} \quad K'_2 = K_1 \sin^2 \theta
\]
Using the angle conventions of Figure 6-1 with Eq 6.7, \( \theta = 0 \) represents no scattering with large \( b \). As \( \theta \) increases, \( v_1' \) and \( K_1' \) decrease until minima are reached at \( \theta = \pi/2 \) where \( v_1' = 0 \) and \( K_1' = 0 \). From Eq 6.9, 6.10 and case II of Table 6.2 this can be seen to represent a head-on collision. By symmetry, deflections in the \(-y\) direction will have the same results so that angles are restricted to \( 0 < |\theta| < \pi/2 \) (bearing in mind that \( K_1' = 0 \) for \( \theta = \pi/2 \)). That is to say, there is no back-scattering of the incident particle for 2-D elastic scattering between equal masses with one particle initially at rest and, from Eq 6.6, the two particles exit the scattering process with velocities at right angles to one-another.

A general solution to Eq 6.4 – 6.6 (\( v_2 = 0 \) but \( m_1 \neq m_2 \) allowed) can be derived following the same procedure as above. Adding the second (squared) forms of Eq 6.4 and 6.5, and substitution using Eq 6.6 arranged for \( m_2^2 v_2^2 \) yields:

**Eq 6.11**

\[
v_1'^2 - \frac{2 \cdot m_1}{(m_1 + m_2)} v_1 \cos \theta \cdot v_1' + \left( \frac{m_1 - m_2}{m_1 + m_2} \right)^2 v_1^2 = 0
\]

Eq 6.11 has the form \( av_1'^2 + bv_1' + c = 0 \), a quadratic equation with well-known solutions.

\[
v_1' = \frac{\frac{2 \cdot m_1 v_1}{(m_1 + m_2)} \cos \theta \pm \sqrt{\left( \frac{2 \cdot m_1 v_1 \cos \theta}{m_1 + m_2} \right)^2 - 4 \cdot \left( \frac{m_1 - m_2}{m_1 + m_2} \right) \cdot v_1^2}}{2}
\]

\[= \frac{m_1 v_1}{(m_1 + m_2)} \cdot \cos \theta \pm \sqrt{\left( \frac{m_2}{m_1} \right)^2 - \sin^2 \theta}
\]

Using \( K_0 = K_1 = \frac{1}{2} m_1 v_1^2 \) to denote the initial kinetic energy (\( v_2 = 0 \) assumed) and noting that \( \cos^2 \theta - \sin^2 \theta = \cos(2\theta) \) (under these conditions, \( K_2' = K_0 - K_1' = \Delta K_1 \)),

**Eq 6.12**

\[
K_1' = \frac{m_1 v_1'^2}{2} = K_0 \cdot \left( \frac{m_1}{m_1 + m_2} \right)^2 \cdot \left[ \cos 2\theta + \left( \frac{m_2}{m_1} \right)^2 \pm 2 \cos \theta \cdot \sqrt{\left( \frac{m_2}{m_1} \right)^2 - \sin^2 \theta} \right]
\]

\[\Rightarrow m_2 < m_1 \Rightarrow \theta_{\text{max}} = \arcsin \left( \frac{m_2}{m_1} \right), \quad 0 \leq \theta_{\text{max}} < \pi/2
\]

When \( m_2 < m_1 \) it is now immediately apparent that real solutions exist only for a limited range of \( \theta \) and that the more massive \( m_1 \) is compared to \( m_2 \), the smaller the range of possible scattering angles. As discussed above for \( m_1 = m_2 \) where \( \theta \) was limited to \( 0 \leq |\theta| < \pi/2 \) on the grounds of symmetry, \( \theta \) is again limited to \( 0 \leq |\theta| < \theta_{\text{max}} < \pi/2 \), where \( \theta_{\text{max}} = \arcsin(m_2/m_1) \). That is, there is
no back-scattering for $m_2 < m_1$. When $m_2 > m_1$ then $\theta$ can take any value, $-\pi < \theta \leq \pi$. The negative root approaches $\theta_{max}$ from a head-on collision while the positive root approaches $\theta_{max}$ from a miss.

Substituting $m_1 = m_2$ into Eq 6.12 using the “+” root of the discriminants yields Eq 6.7 and 6.8 while using the “−” root yields case II (head-on collision), Table 6.2. Likewise, substitution of $\theta = 0$ into Eq 6.12 and 6.13 using the “+” root of the discriminants yields $v'_1 = v_1$ and $K'_1 = K_0 = K_1$, no scattering, while the “−” root yields case I (head-on collision), Table 6.2. When $m_2 >> m_1$, both roots yield $K'_1 \approx K_0 = K_1$; $m_1$ essentially ‘bounces off’ $m_2$ at some angle with very little energy loss. Similarly for $m_1 >> m_2$, $K'_1 \approx K_0 = K_1$ and $v'_1 \approx v_1$ so that $m_1$ essentially ‘ploughs through’ $m_2$, losing almost no kinetic energy and undergoing little to no angular deflection.

Conservation of momentum is built into the centre of mass (CM) reference frame. For non-relativistic situations with $p$ momentum, $m$ mass and $v$ velocity magnitude, $\vec{p} = m\vec{v}$ and:

**Eq 6.13**

$$\left(\sum m_i\right)\cdot \vec{v}_{cm} = \sum m_i\vec{v}_i$$

As long as momentum is conserved and mass remains constant,

**Eq 6.14**

$$K_{cm} = \frac{1}{2}\left(\sum m_i\right)\cdot \vec{v}_{cm}^2 = cons \tan t$$

Conversion from lab frame $\vec{v}$ to velocity in CM coordinates, $\vec{u}$, is through (non-relativistic):

**Eq 6.15**

$$\vec{v} = \vec{u} + \vec{v}_{cm}$$

The relative velocity between 2 particles is the same in lab and CM coordinates,

**Eq 6.16**

$$\vec{u}_1 - \vec{u}_2 = \vec{v}_1 - \vec{v}_2 = \vec{v}_{rel}$$

Returning to 2-particle scattering, under these conditions the angle between $u_1$ and $u_2$ is always $\pi$ due to conservation of momentum, and both $m_1$ and $m_2$ scatter through the same CM scattering angle $\phi$ relative to the x-axis ($\phi_2 = \phi_1 + \pi$), shown in Figure 6-1. Following the earlier notation, $u = -u'$ for elastic scattering in the CM frame. From Eq 6.14,

**Eq 6.17**

$$v_{cm} = \frac{m_1\vec{v}_1 + m_2\vec{v}_2}{m_1 + m_2} \quad u_1 = \frac{m_2}{m_1 + m_2}\vec{v}_{rel} \quad u_2 = \frac{-m_1}{m_1 + m_2}\vec{v}_{rel}$$
When \( m_2 \) is initially at rest, \( v_2 = 0 \), \( v_{rel} = v_1 \) and Eq 6.15 and 6.17 can be used to derive the following conversions for non-relativistic elastic scattering.

**Table 6.3: CM – Lab Frame Conversions for Elastic Scattering with one Particle Initially at Rest**

<table>
<thead>
<tr>
<th></th>
<th>CM Frame</th>
<th>Lab Frame</th>
<th>Lab Frame</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \vec{v}_{cm} )</td>
<td>( \frac{m_1}{m_1 + m_2} v_1 \cdot (1,0) )</td>
<td>( \vec{v}'<em>{cm} = \frac{m_1}{m_1 + m_2} v</em>{cm} \cdot (\cos \phi, \sin \phi) )</td>
<td></td>
</tr>
<tr>
<td>( \vec{u}_1 )</td>
<td>( \frac{m_2}{m_1 + m_2} v_1 \cdot (1,0) = \frac{m_2}{m_1} \vec{v}_{cm} )</td>
<td>( \vec{u}'_1 = u_1 \cdot (\cos \phi, \sin \phi) )</td>
<td></td>
</tr>
<tr>
<td>( \vec{u}_2 )</td>
<td>( -\frac{m_1}{m_1 + m_2} v_1 \cdot (1,0) = -\vec{v}_{cm} = -\frac{m_1}{m_2} u_1 \cdot (1,0) )</td>
<td>( \vec{u}'_2 = \frac{m_1}{m_2} u_1 (-\cos \phi, -\sin \phi) )</td>
<td></td>
</tr>
<tr>
<td>( \vec{v}_1 )</td>
<td>( \left(\frac{m_1}{m_2} + 1\right) u_1 \cdot (1,0) )</td>
<td>( \vec{v}'_1 = u_1 \left(\frac{m_1}{m_2} + \cos \phi, \sin \phi\right) )</td>
<td></td>
</tr>
<tr>
<td>( \vec{v}_2 )</td>
<td>( 0 )</td>
<td>( \vec{v}'_2 = \frac{m_1}{m_2} u_1 \cdot (1 - \cos \phi, -\sin \phi) )</td>
<td></td>
</tr>
</tbody>
</table>

Centre-of-mass (CM) and lab frame velocity magnitudes are \( u \) and \( v \) respectively, and \( \phi \) is the CM scattering angle as shown in Figure 6-1. Conversion was executed using Eq 6.16 and 6.18 (non-relativistic, \( v_2 = 0 \Rightarrow v_{rel} = v_1 \)). Prime superscripts (\( u' \)) denote “after the collision” and un-primed (\( u \)) denote “initial”. The x-axis unit vector \((1,0)\) is aligned with the direction of \( v_1 \) in the lab frame.

Using vector addition and the fact that the x-axis is aligned with \( v_1 \) in the lab frame, \( \vec{v}'_1 \) is the hypotenuse of a triangle that can be employed to convert between the \( m_1 \) scattering angle in the CM and lab frames (see Figure 6-1):

\[
\text{Eq 6.18} \quad \tan \theta = \frac{m_2 \sin \phi}{m_1 + m_2 \cos \phi}
\]

Applying Eq 6.17, the kinetic energy available for conversion or reaction (\( K_R \)) is:

\[
\text{Eq 6.19} \quad K_R = \frac{1}{2} \left(m_1 u_1^2 + m_2 u_2^2\right) = \frac{1}{2} \cdot \frac{m_1 m_2}{m_1 + m_2} v_{rel}^2
\]

When \( v_2 = 0 \), the initial \( K_R \) reduces to:

\[
\text{Eq 6.20} \quad K_R = \frac{m_2}{m_1 + m_2} K_0
\]

where \( K_0 = \frac{1}{2} m_1 v_1^2 \) is the initial kinetic energy in the lab frame. Drawing on Eq 6.14, the conserved kinetic energy is \( K_{cm} = \frac{m_1}{m_1 + m_2} K_0 \) so that \( K_R + K_{cm} = K_0 \) and total energy is indeed
conserved. The more massive $m_2$ is compared to $m_1$, the more energy there is available for reactions or internal excitement, another reason why cooling gases consisting of lighter constituents are often preferred for cooling applications.

After the elastic collision, the kinetic energy of $m_1$ can be expressed by (using Table 6.3):

\[ K_1' = \frac{m_1}{2} (v_1' \cdot v_1') = K_0 \cdot \left( \frac{m_1^2 + m_2^2}{(m_1 + m_2)^2} + \frac{2m_1m_2}{(m_1 + m_2)^2} \cos \phi \right) \]

Here, $v_1' \cdot v_1'$ represents the inner product of the two vectors, $K_0 = \frac{1}{2} m_1 v_1^2$ is the initial kinetic energy in the lab frame and $\phi$ is the CM scattering angle of $m_1$, related to the lab frame scattering angle $\theta$ using Eq 6.18. Then,

\[ \Delta K_1 = K_0 - K_1' = \frac{2 \cdot m_1m_2}{(m_1 + m_2)^2} \cdot (1 - \cos \phi) \cdot K_0 \]

If the collision is not elastic and an amount of kinetic energy, $Q_{col}$, is converted or taken up in a reaction, then Eq 6.19 still remains valid but $v_{rel} \neq v_{rel}'$ and $u \neq u'$. Conservation of energy requires $K_R = K_R' + Q_{col}$ so that from Eq 6.19:

\[ \frac{m_1m_2}{(m_1 + m_2)^2} v_{rel}^2 = \frac{m_1m_2}{(m_1 + m_2)^2} v_{rel}'^2 + Q_{col} \]

\[ \Rightarrow v_{rel}' = \sqrt{\frac{v_{rel}^2 - \frac{2(m_1 + m_2)}{m_1m_2} \cdot Q_{col}}{m_1m_2}} \]

If $Q_{col}$ is small compared to $K_R$ then Eq 6.18 is still approximately valid. For the cases just studied involving $v_2 = 0$ (so $v_{rel} = v_1$), modification of the final velocities in Table 6.3 using Eq 6.17 and $v_{rel}'$ from Eq 6.23 is straightforward. Then, following Eq 6.21 the inelastic process results in (more details can be found in Cooks 1978, p. 252 – 255):

\[ K_1' = \frac{m_1^2 + m_2^2}{(m_1 + m_2)^2} \cdot K_0 - \frac{m_2}{m_1 + m_2} \cdot Q_{col} + \frac{2m_1m_2}{(m_1 + m_2)^2} \cdot K_0 \cos \phi \cdot \sqrt{1 - \frac{Q_{col}}{K_R}} \]

When $Q_{col}/K_R \ll 1$,

\[ K_1' = K_0 \cdot \left[ \frac{m_1^2 + m_2^2 + 2 \cdot m_1m_2 \cos \phi}{(m_1 + m_2)^2} \right] - Q_{col} \cdot \left[ \frac{m_1 \cos \phi + m_2}{m_1 + m_2} \right] - \frac{1}{4} \cdot \frac{m_1}{m_2} \cdot \frac{Q_{col}^2}{K_0} \cos \phi \]

\[ \Delta K_1 = Q_{col} + \frac{m_1}{m_1 + m_2} \cdot (1 - \cos \phi) \cdot \left[ \frac{2 \cdot m_2}{m_1 + m_2} \cdot K_0 - Q_{col} \right] + \frac{1}{4} \cdot \frac{m_1}{m_2} \cdot \frac{Q_{col}^2}{K_0} \cos \phi \]
Setting $Q_{\text{col}} = 0$ in Eq 6.26 and 6.27 returns Eq 6.21 and 6.22 for elastic collisions.

From Eq 6.23 it should be noted that $Q_{\text{col}}$ can result in either an increase or a decrease in $v_{\text{rel}}$. For example, if $Q_{\text{col}}$ were released from a target molecule initially in a vibrational excited state then the projectile may actually gain kinetic energy. On the other hand, a projectile incident on a molecule that not only scatters off of it but also induces a vibrational excited state will leave the collision with even less kinetic energy than if the state were not excited.

Molecular gas targets may also act as ‘softer’ ion coolers than equivalently massive atomic targets. An approaching ion will generally only see part of the molecule due to screening at a distance, and ‘hard collision’ may be between the ion and only one of the molecular constituents. The molecular binding forces may act to buffer the collision, reducing the impact and accelerations involved.

6.2 Cross Sections, Polarizability and Interaction Probability

The most basic approach to calculating a collision cross section between an ion and a neutral atom or molecule is to assume that the two reactants are ‘hard spheres’ of radii $r_1$ and $r_2$ such that for $r < r_x$ the repulsive forces are infinite while for $r > r_x$ the forces are 0. Collision then only occurs at radii $r \leq r_1 + r_2$, and the cross section is simply

\[
\text{Eq 6.28} \quad \sigma_{\text{HS}} = \pi \cdot (r_1 + r_2)^2
\]

Using this model, the mean free path, $\lambda_p$, for an atom or molecule in a monatomic gas is,

\[
\text{Eq 6.29} \quad \lambda_p = \frac{1}{\sqrt{2} \cdot \pi \cdot (2r)^2} \cdot \frac{k_B T}{P}
\]

where $k_B$ is the Boltzmann constant, $T$ and $P$ are the gas temperature and pressure and $r$ is a value for an individual atomic or molecular radius.

Obvious limitations exist, for example vibrating molecules are neither spherical nor fixed in bond length nor ‘hard’ in the sense just used. The model is useful for calculations such as of mean free path and minimum cross section. Often the collision cross section approaches Eq 6.28 at high energy (> 1 eV, non-relativistic) when there is no resonant reaction channel.

On the other hand, the hard sphere approximation does not account for longer range coulomb forces like electron screened nuclear coulomb scattering that would increase the
scattering cross section. At low kinetic energies (typically < 1eV), the influence of the local field of the ion can induce a dipole moment when the neutral is polarisable. When interaction time is sufficient, induced and permanent dipole moments can then increase the interaction time further, affecting scattering angles and collision/reaction cross sections. Examples of cross section variation with kinetic energy can be found in Lindinger et al. (1975), and Sakimoto and Takayanagi (1980) provide a concise discussion of the principles.

More generally, collision cross sections between ions and neutrals are influenced by long-range interaction potentials. In gas phase ion-neutral chemistry at low energy, particularly below 1 eV (eg. Bandura et al. 2001 fig. 7), interaction times are sufficient for induced electric dipole moments to dramatically alter collision cross sections depending on the polarizability ($\alpha$) and permanent dipole moment ($\mu_D$) of the neutral. The resulting induced potentials serve to increase interaction times and help reactants form intermediary complexes.

Raznikov et al. (1999 p. 371) also discuss the case of rebounding that may occur when a relatively massive ion and much less massive neutral interact. If the neutral is not initially captured by the ion but does not have sufficient energy to escape the local field of the ion, the neutral may impact the ion multiple times, resulting in the formation of a quasi-equilibrium state. Eventually the ion may undergo sufficient energy fluctuations and the neutral may be ejected, or energy may be released to the reservoir and leave the ion-neutral system (eg. through collision with another particle) leading to capture. Capture is more likely when the frequency of ion-atom collisions is greater than the expected lifetime of the excited complex.

The Coulomb potential also adds to the potential reaction energy available, and often compensates for reaction channel barriers. Moreover, the absence of solvents or other constituents that may be found in liquid or solid phase chemistry means there are fewer impedances so that reaction rates can be much higher in the gas phase. It should be clear that, in general, cross sections are energy dependant. Resonant reactions, for example electron transfer between two species that have very close energy levels for the electron capture, have very large cross sections over a much larger range of energies.

Langevin (1905) first introduced the electric dipole interaction model to theoretically describe ion mobility in gases, and Gioumousis and Stevenson (1958) later recognized its significance in analyzing ion-gas reaction cross sections. The resultant cross section is variously labeled $\sigma_L$ or $\sigma_{LGS}$:
Eq 6.30

\[ \sigma_{\text{LGS}}(v) = \pi \cdot q \cdot \frac{2 \cdot \alpha}{K_R} \]

\[ \sigma_{\text{LGS}} [\text{cm}^2] = 1.7783804 \times 10^{-15} \cdot (\# \text{charges}) \cdot \sqrt{\frac{\alpha \cdot 10^{-24} \text{cm}^3}{K_R \cdot [eV]}} \]

\( K_R \) is given by Eq 6.19, \( \alpha \) is the polarizability of the neutral, \( q \) is the charge of the ion and the top equation is in cgs units. The expression was derived for collisions (e.g. reactants approach chemically relevant distances) between a point charge and a spherically symmetric neutral.

Rate constants, \( k(E) \), are often quoted, and are related to cross sections by:

Eq 6.31

\[ k(E) = \int P(E) \cdot E \cdot \sigma(E) \cdot dE \approx v_{\text{rel}} \cdot \sigma(E) \]

where the probability of reaction at energy \( E \), \( P(E) \), and the relative speed between the reactants, \( v_{\text{rel}} \), have been introduced. Reduction to \( v_{\text{rel}} \cdot \sigma(E) \) is valid when the energy spread is not large.

With \( \mu = \frac{m_1 m_2}{m_1 + m_2} \), the corresponding LGS rate constant is (cgs units):

Eq 6.32

\[ k_{\text{LGS}} = 2 \cdot \pi \cdot q \cdot \sqrt{\frac{\alpha}{\mu}} \]

Moran and Hamill (1963) then derived what is known as a ‘locked dipole orientation’ (LDO) model to account for permanent dipoles. This tended to overestimate reaction rates and Su and Bowers (1973a, b) then derived an ‘average dipole orientation model’ rate constant, \( k_{\text{ADO}} \).

Eq 6.33

\[ k_{\text{ADO}} = \frac{2 \cdot \pi \cdot q}{\sqrt{\mu}} \cdot \left( \sqrt{\alpha} + C \cdot \mu_D \cdot \frac{2}{\pi \cdot k_B T} \right) \]

Given in cgs units, \( \mu \) is the reduced mass given for Eq 6.32, \( \mu_D \) and \( \alpha \) are the permanent dipole moment and polarizability of the neutral, \( q \) is the charge of the ion, \( k_B \) is the Boltzmann constant, \( T \) is the gas temperature and \( C \) is a constant related to \( \frac{\mu_D}{\sqrt{\alpha}} \) (values can be found in Su and Bowers 1973b, fig. 1 and table 1). When \( C = 1 \), \( k_{\text{ADO}} = k_{\text{LDO}} \) and when \( C = 0 \), \( k_{\text{ADO}} = k_{\text{LGS}} \).

A further modification to ADO theory, known as AADO theory, accounted for angular momentum conservation (Su et al. 1978). More recently, Kummerlöwe and Beyer (2005) have presented a theory to deal with ionic cluster reaction rates. Needless to say, because of the inherently complicated nature of ion-neutral reactions there is great difficulty in accurately calculating each reaction rate theoretically and many theories exist. Those presented here are among the most widely used.
A cross section represents a probability of interaction and, although relatively large compared to other phases, this is generally $<< 1$ for gas phase ion chemistry. Considering a ‘collision’ to be a binary process, the probability that an ion undergoes $x$ collisions while passing through a gas region, $P_c$, can then be described by a Poisson distribution,

$$P_c = \frac{(N \cdot I \cdot \sigma)^x}{x!} \cdot \exp\left(-\left(N \cdot I \cdot \sigma\right)\right)$$

Here ‘!’ is the factorial sign, $N$ is the gas number density (related to pressure and temperature, see Appendix A and Table A 2), $I$ is the length of the region and $\sigma$ is the ion-neutral interaction cross section. The term $N \cdot I \cdot \sigma$ then represents the ‘success’ probability for a ‘collision’.

### 6.3 Reaction Energy and Barriers

When a reaction is exothermic there is an overall decrease in potential energy between reactants and products. This could mean that the two reactants have a strong affinity to bond together, or that one has a stronger affinity for a component of the other (e.g. atom, molecule or electron transfer). Even if a reaction is endothermic, there may be sufficient energy available from kinetic energy ($K_{R}$, Eq 6.19) and Coulomb attraction (as just discussed) to allow the reaction to proceed. Calculations analogous to those in Appendix D can be useful for first-order calculation estimates of whether or not a gas is appropriate for cooling or reacting given $K_R$.

Although there may be sufficient energy available to balance the initial and final requirements for a reaction, potential barriers may exist that inhibit the reaction from happening. Barriers have many sources, such as unfavorable intermediate molecular geometries in going from one species to another or quantum spin configurations (e.g. section 10.3.3). Although after balancing initial and final energy a reaction may appear exothermic or there may appear to be enough energy available to open a reaction channel, it may nonetheless be inhibited from proceeding. Other considerations, such as the fact that ions produced in the majority of ion sources are not thermalized and may be in excited electronic, vibrational and rotational states, must also be accounted for. Some pertinent examples are reviewed by Armentrout (2004).

Let the difference in potential energy between reactants and resultants be denoted $\Delta_b$. When the exothermicity or endothermicity of the reaction is known then $\Delta_b$ is just that energy. When this information is not available then data such as heats of formation ($\Delta_f H$), bond dissociation energies ($D(X–Y)$), electron affinities (EA) and ionization energies (IE) can be used to calculate a value for $\Delta_b$. In the case of electron transfer from an atomic anion ($m_1$) to a neutral
atom (m₂) with associated electron affinities EA₁ and EA₂, Δₐ = EA₁ − EA₂. For a reaction such as \( X^- + YZ \rightarrow XY^- + Z \), \( \Delta_a = EA(X) + D(Y - Z) - D(X - Y) - EA(XY) \) could be used.

Appendices C and D develop analogous ideas in more detail.

When \( \Delta_a < 0 \) the reaction is energetically favourable and should be exothermic, \( \Delta_a > 0 \) means the reaction is endothermic, and \( \Delta_a = 0 \) could mean the reaction is resonant. A threshold energy \( T_e \) can then be defined by:

Eq 6.35

\[
T_e = K_R - \Delta_a
\]

Defined in this way, \( T_e < 0 \) means the process is not energetically favourable and \( T_e \geq 0 \) means there is enough energy available for the process to take place. Equation 6.35 does not describe exothermicity or whether the reactant relative velocity is favourable for the reaction, only whether there is sufficient kinetic energy to fulfil basic energy requirements for reaction.

As an example, consider Cl (EA_{Cl} = 3.612724 eV), Ar (EA_{Ar} ≈ 0) and NO₂ (EA_{NO₂} = 2.273 eV) (Haynes and Lide 2011). To first order, electron detachment from Cl⁻ would require \( \Delta_a > 3.61 \) eV while electron transfer, Cl⁻ + NO₂ \( \rightarrow \) NO₂⁻ + Cl, would be endothermic by only \( \Delta_a(EA(Cl-NO₂)) = 1.34 \) eV. Using 46, 40 and 35 amu as the masses of NO₂, Ar and Cl, for the same lab frame incident kinetic energy, \( K_0 \), the energy available for reaction, \( K_R \) (Eq 6.19), is larger for Cl⁻ on NO₂ than for Cl⁻ on Ar by \( \sim 5\% \) because NO₂ is larger in mass. Then, electron detachment may be estimated to begin at \( K_0 = 6.8 \) eV for Cl⁻ on Ar and 6.36 eV with NO₂. However, there may be additional Cl⁻ losses at only \( K_0 = 2.36 \) eV with NO₂ from electron transfer and this would need to be considered when designing an experiment.

These calculations are, of course, very simplistic and do not account for the quantum nature of the systems involved. For example, Smith et al. (1978) measured electron detachment cross section threshold kinetic energies (lowest energy at which significant cross section is observed) for Cl⁻ and Br⁻ on rare gases to be twice the respective electron affinities, \( K_R \sim 2 \times EA \) (CM frame). Similarly, the electron detachment threshold energy for F⁻ + He has been measured to be \( K_R = 6.15 \) eV \( \sim 1.8 \times EA(F) \) (Huq et al. 1982). This would not be predicted by Eq 6.35.

6.3.1 Application to the Oak Ridge RF Quadrupole Isobar Separator

Of particular interest is recent work with an rf quadrupole cooler for anions produced from Cs⁺ sputter sources (Liu et al. 2002, 2007, 2009). After acceleration to several keV, the anion beam is filtered using standard MS techniques for injection into the cooling system. Deceleration to tens of eV kinetic energy is accomplished using a 7-electrode ‘ring electrode’,
leading directly into the cooler through a $\phi 3$ mm ($\phi$ is diameter) aperture. The rf quadrupole is 40 cm long with inscribed radius $r_0 = 3.5$ mm (Figure 4-1), operating at $f = 2.75$ MHz using static voltage ‘gradient bars’ to maintain forward ion motion and exit aperture of $\phi 2$ mm. Ring electrode ion guides are discussed in Tolmachev et al. (2000). Cooling the ions to reduce the radial displacement and confine them on-axis was meant to increase transmission and provide a larger density of ions for interaction with laser beams for photodetachment of electrons from unwanted isobars. The slower ions also have a longer interaction time with the photons.

Based on initial cooling studies and modelling, the system was optimized for ion deceleration to 40 eV lab frame kinetic energy before cooling with He at room temperature. Deceleration to $< 40$ eV was found to produce too much additional ion beam divergence. Greater divergence increases the radial kinetic energy component, $K_r$, which can limit the rf quadrupole instrument transmission as discussed in chapter 5.

Modifications were made to increase the differential pumping between cooler and acceleration regions after experiments showed large anion attenuations due to electron detachment from collisions at high energy (Liu et al. 2007). Table 6.4 presents transmission data with the modified system (Liu et al. 2009) using ~ 50 mTorr He in the cell. Using Eq 6.20, $K_R$ was calculated with $m_1$ the anion mass, $m_2 = 4$ amu for He and $K_0 = 40$ eV. Since $E_A_{He} = 0$, $\Delta b = E_A_{1}$ and $T_e = K_R - E_A_{1}$ for electron detachment.

The electron detachment threshold energy (CM frame) for O$^-$ + He has been measured to be slightly below $D_0(e) = 4$ eV (Penet et al. 1987 fig. 4a), and those of Cl$^-$ + He and F$^-$ + He to be $D_0(e^-) = 7.1 \pm 0.1$ eV and $6.15 \pm 0.15$ eV respectively (Smith et al. 1978, Huq et al. 1982). Figure 6 in Liu et al. (2007) shows transmission vs. $K_R$ data for O$^-$ and F$^-$ + He consistent with this. Table 6.5 presents the same transmission data for O, F and Cl but uses $\Delta b = D_0(e)$ instead of $\Delta EA$ for $T_e$ calculation.

The $D_0(e)$ values correspond to laboratory frame $K_0 = 20$ eV (O), 68 eV (Cl) and 35 eV (F). Clearly at $K_0 = 40$ eV, O$^-$ is well above the threshold energy, F$^-$ is close to but above threshold, and Cl$^-$ is well below the threshold energy. It is reasonable to suggest, as discussed in Liu et al. (2007), that electron detachment due to high energy collisions with residual gas leaking from the cell are still responsible for a large proportion of ion losses. Other losses may also arise from scattering.

Another mechanism of loss is likely excessive rf heating (section 4.1.2). Taking Cl$^-$ data, it seems that the cell was operated around $V_{0p} = 150$ V during measurements (Liu et al. 2009, p.
Using the cell parameters, \( q_2 = 0.452 \) (Eq 4.19) which is rather large for cooling. A \(^{35}\)Cl\(^-\) ion entering on the perimeter of the \( \phi 3 \) mm entrance aperture will experience an effective potential, \( V^*(r = 1.5 \text{ mm}) = 3.1 \text{ eV} \) (Eq 4.40). From Eq 4.42, this translates into 6.1 eV rf heating (using \( v_{21}^2 = 0.2 \), see Appendix G). An ion entering at \( r = 1 \) mm would experience \( V^*(r = 1 \text{ mm}) = 1.4 \text{ eV} \), for 2.7 eV rf heating. Combined with the radial energy of the ion (likely large from a sputter source and augmented from beam divergence during deceleration), the potential of the rf field alone (\( v_{22}^2 = 1.18 \) for heating contribution, see Appendix G) could easily add enough energy to exceed the electron detachment threshold energy in the radial direction.

All \( T_e \) values calculated using EA are positive (electron detachment is energetically favorable) while calculation using \( D_0(e) \) shows \( e^- \) detachment from Cl\(^-\) to be energetically very unfavorable. Transmission vs. \( T_e \) using both calculation methods is plotted in Figure 6-2.

From Table 6.4, transmission is not correlated with EA, mass or \( K_R \) alone, but ordering from largest to least transmission correlates with least to largest \( T_e \). There is also a strong linear agreement between transmission and \( T_e \) calculated using EA, shown in Figure 6-2 (blue squares).

While transmission order correlates with both \( D_0(e) \) and \( T_e \), a plot of \( D_0(e) \) vs. transmission does not yield a good linear relationship while, perhaps not surprisingly, the plot of transmission vs. \( T_e \) (calculated using \( D_0(e) \)) does since \( T_e \) includes the energy available for conversion. Although there are only 3 data points for \( D_0(e) \) calculations, there is agreement between 7 data points using EA and this suggests that there may be a similarly strong correlation between the electron affinities of the elements studied and their anion threshold electron detachment energies with He. It also seems reasonable that, since Figure 6 from Liu et al. (2007) shows transmission peaks vs. \( K_R \) data for O\(^-\) and F\(^-\) + He consistent with the previously cited \( D_0(e) \), that a rough prediction of \( D_0(e) \) for the other anions on He should be possible.

From Figure 4 in Liu et al. (2007), the ion beam energy spread for Ni\(^-\) and Co\(^-\) can be approximated as 4 – 6 eV (at full width half maximum and at the base of linear-linear plots). Energy spreads for Cl\(^-\) and F\(^-\) are likely larger and it would be reasonable to approximate an energy uncertainty of at least \( \Delta K_0 = \pm 3 \) eV, or \( \Delta K_R = 7.5\% \), dominating the uncertainty in the \( D_0(e) \) of Table 6.5 used in calculations of \( T_e \) (Eq 6.35). With this in mind, \( D_0(e) \) for \(^{32}\)S\(^-\), \(^{58}\)Ni\(^-\), \(^{59}\)Co\(^-\) and \(^{64}\)Cu\(^-\) on He may be approximated from the slope of the linear fit in Figure 6-2 as:

\[
D_0(e) = K_R - \left( \frac{Tr - 39.85179}{-3.91849} \right)
\]

where \( Tr \) is the transmission given in Table 6.4.
Results are given in Table 6.6 and uncertainty calculations are described in the caption. This calculation is particular to the system used for measurements and would not apply to a set of data from an arbitrary rf quadrupole system. Furthermore, these are certainly not based on careful single collision measurements and the energy spread of the ion beam has not been accounted for. However, the calculation should provide a rough guide to the D₀(e) of the listed anions with He.

Table 6.4: Transmission Data from Oak Ridge rf Quadrupole Cooling Instrument

<table>
<thead>
<tr>
<th>Ion</th>
<th>Neutral Mass (amu)</th>
<th>Transmission (%)</th>
<th>Transmission Uncertainty (± %)</th>
<th>EA (eV) (−Δ₀)</th>
<th>Kᵣ (eV)</th>
<th>Tₑ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>35</td>
<td>51</td>
<td>8</td>
<td>3.6173</td>
<td>4.10</td>
<td>0.49</td>
</tr>
<tr>
<td>Cu⁻</td>
<td>64</td>
<td>52</td>
<td>11</td>
<td>1.2281</td>
<td>2.35</td>
<td>1.12</td>
</tr>
<tr>
<td>Ni⁻</td>
<td>58</td>
<td>52</td>
<td>12</td>
<td>1.1561</td>
<td>2.58</td>
<td>1.42</td>
</tr>
<tr>
<td>Co⁻</td>
<td>59</td>
<td>43</td>
<td>13</td>
<td>0.6611</td>
<td>2.54</td>
<td>1.88</td>
</tr>
<tr>
<td>S⁻</td>
<td>32</td>
<td>45</td>
<td>5</td>
<td>2.0771</td>
<td>4.44</td>
<td>2.37</td>
</tr>
<tr>
<td>F⁻</td>
<td>19</td>
<td>38</td>
<td>8</td>
<td>3.3993</td>
<td>6.96</td>
<td>3.56</td>
</tr>
<tr>
<td>O⁻</td>
<td>16</td>
<td>24</td>
<td>4</td>
<td>1.4611</td>
<td>8.00</td>
<td>6.54</td>
</tr>
</tbody>
</table>

Transmission data are taken from Liu et al. (2007, 2009) for transmission through a collision cell used for cooling anions (described in the text, section 6.3.1). Anions are decelerated to 40 eV before the injection aperture to the collision cell for cooling in He gas at room temperature. Kᵣ is the available kinetic energy for conversion, calculated from Eq 6.20 using K₀ = 40 eV, m₁ = anion neutral mass, m₂ = 4 amu (for He). Tₑ is the threshold energy for electron detachment during anion–He interactions (Eq 6.36). Electron affinities (EA) are from Haynes and Lide (2011). Since EA(He) = 0, Δ₀ = −EA(anion) was used for Tₑ calculations. The list is ordered from largest to least transmission which correlates with least to largest Tₑ but not with EA (−Δ₀) or Kᵣ separately.

Table 6.5: Transmission Data from Oak Ridge using Threshold Electron Detachment Energy for Tₑ Calculation

<table>
<thead>
<tr>
<th>Ion</th>
<th>Neutral Mass (amu)</th>
<th>Transmission (%)</th>
<th>Transmission Uncertainty (± %)</th>
<th>D₀(e) (eV) (Δ₀)</th>
<th>Kᵣ (eV)</th>
<th>Tₑ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>35</td>
<td>51</td>
<td>8</td>
<td>7.1 ± 0.1</td>
<td>4.10</td>
<td>-3</td>
</tr>
<tr>
<td>F⁻</td>
<td>19</td>
<td>38</td>
<td>8</td>
<td>6.15 ± 0.15</td>
<td>6.96</td>
<td>0.81</td>
</tr>
<tr>
<td>O⁻</td>
<td>16</td>
<td>24</td>
<td>4</td>
<td>4</td>
<td>8.00</td>
<td>4</td>
</tr>
</tbody>
</table>

Values as in Table 6.4 with D₀(e) the experimentally measured threshold electron detachment energies on He from: Penet et al. (1987, O⁻), Smith et al. (1978, Cl⁻), Huq et al. (1982, F⁻).
Transmission data are taken from Liu et al. (2009) for transmission through a collision cell used for cooling anions (described above in section 6.3.1). Anions are decelerated to 40 eV before the injection aperture to the collision cell for cooling in He gas at room temperature. $T_e$ is given by Eq 6.35 and is calculated using (blue squares) $\Delta_b = \Delta EA$ (electron affinity, see Table 6.4) and (black open circles) $\Delta_b = D_0(e)$ (threshold energy for electron detachment given in references, see Table 6.5). Linear fits were calculated using Origin 7.5.

### Table 6.6: Estimated Electron Detachment Threshold Energies of $^{32}$S$^-$, $^{59}$Ni$^-$, $^{59}$Co$^-$ and $^{64}$Cu$^-$ on He

<table>
<thead>
<tr>
<th>Anion</th>
<th>$D_0(e)$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{32}$S$^-$</td>
<td>5.8 ± 0.4</td>
</tr>
<tr>
<td>$^{59}$Co$^-$</td>
<td>6.0 ± 0.4</td>
</tr>
<tr>
<td>$^{58}$Ni$^-$</td>
<td>3.3 ± 0.5</td>
</tr>
<tr>
<td>$^{64}$Cu$^-$</td>
<td>5.5 ± 0.4</td>
</tr>
</tbody>
</table>
Transmission data from Liu et al. (2007, 2009) for anion transmission through an anion cooler (discussed above) was used with experimentally measured threshold electron detachment values ($D_0(e)$) for Cl, F and O on He (see Table 6.5 and text) to calculate $T_e$ (Eq 6.35) and is plotted in Figure 6-2. A linear fit through the data with data from Table 6.4 was used to determine Eq 6.36, the values in this table. The strong linear relationship between $T_e$ and transmission calculated using electron affinities (EA, Figure 6-2 blue squares), the good linear fit using $D_0(e)$, although only through 3 points, and other experimental data from Liu et al. (2007) suggested Eq 6.36 may be a reasonable guide. Uncertainties were calculated in the usual fashion, $\sqrt{\sum (\Delta a/a)^2}$, using the linear fit uncertainties, $\Delta K_R = 7.5\%$ and the transmission uncertainties listed in the tables, and then divided by the correlation coefficient of the fit.

### 6.4 Some Notes on Cooling Gas Selection

Use of molecular gases for cooling instead of atomic may result in greater average energy loss per collision since rotational or vibrational modes may be excited, taking advantage of $Q_{\text{col}}$ from Eq 6.26. Molecules with more degrees of freedom may be able to cool more per collision. However, if the gas were composed of atoms or molecules massive compared to the incident ion, there would be more energy available for conversion, $K_R$ (Eq 6.19), possibly leading to unwanted reactions or electron detachment, and a larger range of available scattering angles to the projectile, possibly leading to unwanted scattering losses. Values of maximum kinetic energy loss and the kinetic energy available for conversion, $\Delta K$ and $K_R$, during elastic collisions in the hard sphere approximation are plotted in Figure 6-3. The drop in $\Delta K/K_0$ shown above $m_2/m_1 = 1$ corresponds to $m_1$ recoiling energy for head-on collisions. For $m_2/m_1 > 1$, all scattering angles are possible.

Molecules consisting of less massive atoms may also act as ‘softer’ targets compared to equivalently massive molecules with more massive atomic constituents. An incident ion will interact with the outermost atoms first and some of the impact can be taken up by the molecular bond. Furthermore, molecules that are highly polarisable or have large dipole moments will have larger interaction cross sections at low energy. On the other hand, this may promote unwanted ion-neutral adduct formation. Also, as discussed in section 6.2, a relatively small anion may be trapped by the coulomb interaction with a much larger molecule leading to unwanted losses.

If no reactions are desired, gases that do not react with the ion should obviously be chosen. As discussed in section 6.3, it is also important to consider kinetic energy as unwanted
endothermic reaction channels may be accessible if the initial ion energy were too large. As a first order approximation, Eq 6.35 can be used while considering different reaction pathways.

**Figure 6-3: Hard Sphere Elastic $\Delta K$ and $K_R$ vs. Mass Ratio of Projectile and Target**

The change in kinetic energy ($\Delta K$, Eq 6.22) of a projectile, $m_1$, in an elastic collision with a target, $m_2$, initially at rest in the hard sphere approximation is plotted against the mass ratio of the two particles. Values are given for maximum kinetic energy loss from $m_1$ (a head-on collision, $\phi = \pi$ in the centre of mass, CM, frame) and half the maximum kinetic energy loss ($\phi = \pi/2$ in the CM frame). Also plotted is the energy available for conversion, $K_R$ (Eq 6.20), during the collision. Values are normalized to the initial kinetic energy of $m_1$ in the lab frame, $K_0$. 
7 Experimental System

Figure 7-1: Schematic Drawing of the ISA Test Bed and AMS System at IsoTrace Laboratory

The region from the 860 Cs\(^+\) negative ion source up to and including AA is the ISA test bed. Anions were typically accelerated to 20 keV at the source. However, for some larger molecular anion studies this was reduced to 10 keV due to limitations of the maximum field available from magnet 1. For details on accelerator mass spectrometry and mass spectrometry in general see chapter 2 and Figure 2-1. Slits will be referenced by: vertical top (T), bottom (B); horizontal by position (N, E, W, S, top of figure; FC6 only has horizontal N/S slits), the opening representing the slit distance from the z-axis.

Figure 7-1 shows the major components of the AMS system used (for further details see Kilius et al. 1987, 1990). The section from sputter source up to and including AA is the ISA test bed.

Negative ions were produced using an 860 type inverted Cs\(^+\) ion sputter source and typically accelerated to 20 keV axial kinetic energy (for details on this type of source see
The sputter target was always set to \(-4\) kV for Cs\(^+\) acceleration and initial ion acceleration, with the ion source deck typically set at \(-16\) kV for total anion acceleration to \(20\) keV. The anion beam was then analyzed in a wide gap (80 mm), 90°, 500 mm radius magnet and then focussed onto a \(\phi2\) mm (\(\phi\) is diameter) aperture located at the focal plane of the magnet. A \(\phi10\) mm aperture was placed between the magnet exit and the focal plane (500 mm upstream from the 2 mm aperture), limiting the beam’s on-axis angular spread at the 2 mm aperture to within ±10 milli radians (mr) before injection into the ISA. This divergence is relatively small for a typical AMS system. Due to limitations of the maximum available magnetic field from magnet 1, some experiments involving molecular ions required the source voltage to be reduced (see Table 2.1).

The ISA was housed in a vacuum chamber (described in section 7.1) that was electrically isolated and maintained at a negative high voltage slightly lower in magnitude than the full acceleration potential of the ion source. The source-ISA voltage difference is,

\[
\Delta V_{\text{ISAS}} = V_{\text{ISA}} - V_S
\]

where \(V_{\text{ISA}}\) and \(V_S\) represent the ISA deck and ion source voltages. Defined in this manner, \(\Delta V_{\text{ISAS}} > 0\) when \(V_S < V_{\text{ISA}} < 0\). Using \(q = |ne| = 1\) for anions, \(q \cdot \Delta V_{\text{ISAS}}\) represents the minimum kinetic energy of the ions with respect to the ISA deck that can be achieved electrostatically. It was found that transmission decreased rapidly below \(\Delta V_{\text{ISAS}} \sim 4\) eV (eg. see Figure 8-1) so that \(\Delta V_{\text{S/ISA}} = 5 - 15\) V typically. Additional energy loss could be achieved through cooling. High precision resistor divider networks were used as input to a Keithley 2100 6½-digit Multimeter (Keithley Instruments Inc., Cleveland, Ohio, U.S.A.) to independently measure \(V_S\) and \(V_{\text{ISA}}\) to a relative accuracy of 1.3 – 1.0 V for \(-20\) kV \(\leq V_S\) and \(V_{\text{ISA}} \leq -15\) kV (more details in section 7.2).

After exiting the ISA, ions were re-accelerated by the deck voltage, \(V_{\text{ISA}}\), typically to about 20 keV. Following the ISA was another vacuum chamber (AA Figure 7-1) that housed an electron multiplier, Faraday cup (FC3) and steerer set on a linear track, transverse to the beam axis, so that they could variously be placed in the path of the reaccelerated ions. The steerer set was used to help steer the ions for measurement by FC4 or for injection into the tandem accelerator for analysis by accelerator mass spectrometry (AMS, described in chapter 2).

There was a 500 mm ‘dead zone’ in the ISA chamber following re-acceleration that was shielded with a perforated (for pumping) metal jacket to maintain the inner region at ground potential (see Figure 7-4 for ISA schematic). A magnet was placed on the ISA chamber lid mid-
way along this section for electron suppression. Significantly, this area would have been at relatively high pressure when gas was used in the ISA, facilitating high energy ion-gas interactions and possible unwanted ion loss or production.

### 7.1 Test Bed Vacuum System and Pressure Monitoring

Refer to Figure 7-1 for meanings of component name short-forms and positions. A Varian Turbo V200 turbine pump (220 l/s N₂, 210 l/s He, 180 l/s H₂; currently Varian Inc. is part of Agilent Technologies, Santa Clara, California, U.S.A.) and Leybold-Heraeus GmbH Turbovac 150 turbine pump (145 l/s N₂; currently Oerlikon Leybold Vacuum GmbH, Cologne, Germany) were located at 600 mm and 813 mm from the ion source (under FC1). A Leybold-Heraeus GmbH Turbovac 1000 turbine pump (850 – 1150 l/s N₂; ibid) was located roughly mid-way between FC1 and the entrance to magnet 1, ~ 310 mm from the 150 turbo pump and ~ 270 mm from the magnet entrance.

The ISA was housed in a rectangular aluminum vacuum chamber with dimensions: length 935 mm (along anion trajectory), width 204 mm (face through which anions passed) and height 215 mm. Centred at 584.2 mm from the entrance (~ 2/3 the length) was a φ177.8 mm (7") pumping channel. An identical chamber was used between magnet 1 and the ISA. Each chamber was pumped directly by a CTI Cryotorr 8 cryopump (4000 l/s H₂O, 1500 l/s air, 2500 l/s H₂, 1200 l/s Ar; CTI Cryogenics, Brooks Automation Inc., Chelmsford, Massachusetts, U.S.A).

Chamber AA was rectangular with dimensions: width 150 mm (N – S dimension with directions defined in Figure 7-1 at ‘East Wall’), length 406.4 mm (E – W dimension) and height 158 mm. Pumping was through a Leybold TW 250 turbomolecular pump (230 l/s N₂; company details above) that was attached horizontally to one side of the chamber.

A φ25.4 mm (1") cylinder was used at the ISA chamber entrance and a 200 mm long, φ60 mm cylinder with φ25.4 mm (1") entrance and exit apertures at the ISA chamber exit were used to restrict gas flow out of the ISA chamber and protect the electrical isolation insulators from ion and electron bombardment. Typically chamber AA was an order of magnitude lower in pressure than the ISA chamber when gas was leaked into the collision cell.

Pressure was monitored at FC1 (‘PFC1’), in the centre of a side face of the ISA chamber (roughly where the collision cell is located, ‘Pisa’) and at the pumping orifice for chamber AA (‘PFC3’) using PKR 250 Balzers compact full range pressure gauges (now Oerlikon Balzers,
Balzers, Liechtenstein). Collision cell pressure was also monitored independently. Pressure for the tandem accelerator stripping canal was not measured directly. Instead, it could be inferred from the ‘low energy pressure’ (‘PLE’ at FC4) and ‘high energy pressure’ (‘PHE’ just after the 45° EA) as measured by PKR 250 Balzers gauges (ibid).

### 7.2 Deck High Voltage Measurement ($V_s$, $V_{ISA}$ and $\Delta V_{ISAS}$)

For multimeter manufacturers and specifications see Figure 7-2.

The ion source deck and ISA chamber voltages were monitored separately using the Keithley 2100 6 1/2-Digit Multimeter. Attached to each deck was a low-current circuit with a ‘step down’ ratio of ~ 2390 : 1, as illustrated in Figure 7-2, so that deck voltages (typically < −21 kV) could be monitored using the 10 V range scale. Given the quoted accuracy in this range, a −20 kV deck voltage would be ‘stepped down’ to −8.36820 V (neglecting the ‘step-down’ circuit resistance uncertainty), which could be read to an accuracy of 0.00038 V (or 0.0045 %) by the Keithley meter. This represents a measurement uncertainty of 0.9 V for −20 kV.

**Figure 7-2: ‘Step-down’ Resistor Circuit and Multimeter Information**

To produce a ‘step-down’ resistor circuit, two resistors $R_1$ and $R_2$ can be connected in series between a power supply, $HV_d$, and ground. The current, $I$, through each resistor is the same so that the voltage drop across $R_2$, $V_K$, is related to $HV_d$ through the equation shown. The high voltage on the ISA chamber ($V_{ISA}$) and Cs⁺ sputter source deck ($V_s$) were measured as $V_K$ with $R_1 = 200 \pm 2 \, \text{M} \Omega$, $R_2 = 83.80 \pm 0.02 \, \text{k} \Omega$ for a step down ratio of $4.19 \pm 0.04 \times 10^{-4}$, or $(2387 \pm 24) : 1$.

<table>
<thead>
<tr>
<th>Multimeter</th>
<th>Manufacturer</th>
<th>Quoted Accuracies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Keithley 2100 6 1/2-Digit</td>
<td>Keithley Instruments Inc., Cleveland, Ohio, U.S.A.</td>
<td>Voltage (0 – 10 V range): 0.0038% x reading + 0.00006 V</td>
</tr>
<tr>
<td>Fluke 189 True RMS</td>
<td>Fluke (Canada head office), Mississauga, Ontario, Canada</td>
<td>Voltage (dc): 0.025% Resistance: 0.05%</td>
</tr>
</tbody>
</table>
In the ‘step-down’ circuit, resistor ‘R1’ was a high precision 200 ± 1% MΩ ceramic resistor (MG 815N – 15; Caddock Electronics Inc., Riverside, California, U.S.A.). Resistor R2 was composed of 2 ceramic resistors (Ohmite “Little Devils”, resistance uncertainty of 2%, Welwyn Components Ltd, Bedington, Northumberland, U.K.) soldered in series to produce 83.80 ± 0.04 kΩ resistance as measured using the Fluke 189 True RMS Multimeter. Each circuit then had a ‘setp-down’ ratio of (2387 ± 24) : 1 (± 1%, see Figure 7-2 for equations). Circuit were calibrated as described in section 7.2.1.

Copper AWG 18 wires (Belden 8501 – 1000 VW–1; Belden, St. Louis, Missouri, U.S.A.) of length 1067 mm ISA / 1168 mm source were screwed onto the ISA deck and source sample arm (where full ion acceleration voltage is applied), and soldered to R1. Coaxial cable (Belden 8254 RG58AU; company details above) of length 3962 mm ISA / 4674 mm source were screwed to the other R1 connection, with R1 and the connections housed in a plexiglass sheath. The midpoint of the sheath was fastened in such a way that the high voltage connection was above the deck (sitting in the high voltage region) while the other was below (in the ‘ground’ voltage region). The other coaxial cable connection was to the R2 resistor series, housed in an aluminum box. Both box and coaxial shielding were connected to the appropriate high voltage ground node.

A second coaxial cable (ibid) of length 3962 mm ISA / 4674 mm source had its shielding connected to the appropriate deck ground node and the wire to the R1 – R2 connection for measurement of V_K (Figure 7-2). Wire resistance is negligible compared to the resistances used so that the division was 1/(2387 ± 24) (± 1%, see previous paragraph).

### 7.2.1 Resistor Circuit Calibration and Measurement Uncertainties

Both resistor chains were attached to the ISA deck simultaneously for calibration, and voltage outputs were measured with the Keithley meter. The Fluke meter with a 1000:1 (± 2%) voltage divider grounded to the ISA ground node (80k–40 H.V. Probe; Fluke, ibid) monitored the ISA deck voltage independently. The Fluke readings were used as an absolute reference value for the deck voltage against which the Keithley readings from the resistor chains were compared. One resistor chain was designated for use with the ion source and the other for use with the ISA.

With this configuration, both resistor chain outputs (as measured on the Keithley meter) were simultaneously compared to the single output of the Fluke meter, used as an absolute
reference, and likewise compared to one-another. Let $V_F$ represent the Fluke meter reading, $V_{KS}$ represent the Keithley meter reading for the ion source resistor chain and $V_{KISA}$ represent the Keithley meter reading for the ISA resistor chain. Let the voltage ‘step-down’ factor of the ion source resistor chain be $\chi_S$ and that of the ISA resistor chain be $\chi_{ISA}$. Then, during these measurements,

$$V_F = \frac{V_{KS}}{\chi_S} = \frac{V_{KISA}}{\chi_{ISA}}$$

In this way, with $V_F$ an absolute voltage reference, the uncertainty of the respective ‘step-down’ factors, $\chi$, were no longer dependent on the resistor circuit resistor value uncertainties but rather on the Keithley meter accuracy.

The ISA deck was then set to $-20$ kV, left to warm up for 12 hours and then scanned over the range $-15$ kV to $-20.7$ kV in steps of $0.5$ kV from $-15$ kV to $-20.1$ kV, and then in steps of $0.05$ kV for the remainder of the interval. Over the course of experiments reported in this thesis, this was the range of deck voltages used. Corresponding Keithley readings ranged from $-5.98$ V to $-8.28$ V which could be measured to accuracies of $0.0048\%$ and $0.0045\%$ respectively (see Figure 7-2).

Values of $\chi_{ISA} = V_{KISA}/V_F$ and $\chi_S = V_{KS}/V_F$ were calculated from the average values, $<\chi_{ISA}>$ and $<\chi_S>$, of the $N = 25$ measurements,

$$\chi_{ISA} = 3.9992 \cdot (3) \times 10^{-4}$$
$$\chi_S = 3.9832 \cdot (3) \times 10^{-4}$$

The number in brackets represents the uncertainty in the last digit and was calculated from the measurement variance, $s = \sqrt{\frac{\sum_{i=1}^{N} (\chi_i - <\chi>)^2}{N-1}}$ (described further in Bevington 1969), representing an uncertainty of $0.0075\%$. However, the Fluke meter was not as accurate as the Keithley meter.

When calculating deck voltage offsets, $\Delta V_{ISAS}$ (Eq 7.1), a more appropriate measure of the relative $\chi$ value uncertainties is to consider the average ratio, $<V_{KISA}/V_{KS}> \equiv <\chi_{ISA}/\chi_{KS}>$, over the series of measurements and use the variance of these data for the relative $\chi$ uncertainties. These ratios were measured to higher accuracy and are more representative of the actual experimental conditions. This was determined to be,

$$\left\langle \frac{V_{KISA}}{V_{KS}} \right\rangle \equiv \left\langle \frac{\chi_{ISA}}{\chi_{KS}} \right\rangle = 1.004020 \cdot (5)$$
As above, the number in brackets represents the uncertainty in the last digit as calculated from the measurement variance. The uncertainty is 0.0005%.

With these values for \( \chi \), the ISA and ion source deck voltages could be calculated by:

\[
V_{ISA} = \frac{V_{KISA}}{0.000399922}
\]

\[
V_S = \frac{V_{KS}}{0.000398321}
\]

Eq 7.2

Here, \( V_{ISA} \) and \( V_S \) represent the deck voltages as used for Eq 7.1. Values with a subscript ‘K’ represent the voltages as read from the Keithley meter with appropriate ‘step-down’ resistor chain (notation as used above). Uncertainty in the denominators of Eq 7.2 is \( 5 \times 10^{-9} \) based on the \( \frac{V_{KISA}}{V_{KS}} \equiv \frac{\chi_{ISA}}{\chi_S} \) given above. Voltages ranging from \(-15 \text{ kV} \) to \(-20 \text{ kV} \) could be determined with uncertainties ranging from 0.0048% to 0.0045% as determined from the percent uncertainties given above for the Keithley meter (\( \sigma_K \)) and \( \chi \) values (\( \sigma_\chi \)) through \( \sqrt{(\sigma_K)^2 + (\sigma_\chi)^2} \).

This corresponds to \( \pm 0.72 \text{ V} \) to \( \pm 0.90 \text{ V} \). Uncertainty in the calculation of the offset between the two decks, \( \Delta V_{ISAS} \) (Eq 7.1), then ranged from \( \pm 1.0 \text{ V} \) for the decks near \(-15 \text{ kV} \) to \( \pm 1.3 \text{ V} \) for the decks near \(-20 \text{ kV} \).

### 7.3 Ion Flux Measurements

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Useful Range</th>
<th>Manufacturers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Keithley 414A Picoameter</td>
<td>&gt; 0.1 nA</td>
<td>Keithley Instruments Inc., Cleveland, Ohio, U.S.A.</td>
</tr>
<tr>
<td>Keithley 414S Picoameter</td>
<td>&gt; 0.1 nA</td>
<td></td>
</tr>
<tr>
<td>Keithley 610B Electrometer</td>
<td>&gt; 0.01 pA</td>
<td></td>
</tr>
<tr>
<td>Gas Ionization Detector with Canberra 1480 Linear Ratemeter</td>
<td>50 q/s – 55 000 q/s</td>
<td>Canberra, Meriden, Connecticut, U.S.A.</td>
</tr>
<tr>
<td>Gas Ionization Detector with Canberra multichannel analyzer (see Figure 7-3)</td>
<td>1 q/5 hrs – 5000 q/s</td>
<td>Designed and build by Dr. Xiao-Lei Zhao, IsoTrace Laboratory</td>
</tr>
</tbody>
</table>

‘q’ represents ‘charge’ (q = 1 for a singly charged ion), ‘s’ represents ‘second’, ‘hrs’ represents ‘hours’. Sensitive measurements were taken either with the 610B electrometer or the gas ionization detector.
The electron multiplier in chamber AA was not used. Faraday cups FC2, FC3 and FC7 were suppressed by -50 V, -100 V and -300 V respectively and used for sensitive measurements. Table 7.1 lists the instruments used to read the ion fluxes. Figure 7-3 gives a schematic of the ionization chamber employed and describes the general principles. Experimental values for the voltages V1, V2 and V3, and the isobutane (C₄H₁₀) pressure are given in Table 7.3.

**Figure 7-3: Gas Ionization Detector Schematic**

<table>
<thead>
<tr>
<th>Window 12 mm [0.47&quot;]</th>
<th>90 mm [3.55&quot;]</th>
<th>V1</th>
<th>90 mm [3.55&quot;]</th>
<th>V2</th>
<th>3 mm [0.10&quot;]</th>
</tr>
</thead>
</table>

Ions entered the detector chamber through a φ12 mm, 120 μg/cm² polypropylene window. Two sets of electrodes (red) held at voltages V1 and V2 relative to the top of the chamber collected ionization signals. The base of the chamber was grounded and the gap between the electrodes was set to voltage V3. Isobutane (C₄H₁₀) was used as the ionization gas and ions were generally stopped in the region of V1 with 15 – 20 Torr gas pressure for the experiments described.

The signals from the electrodes were first amplified by an Ortec 142AH preamplifier (Ortec Products Group, Oak Ridge, Tennessee, U.S.A.), then by a Canberra 2022 amplifier (Canberra, Meriden, Connecticut, U.S.A.). This was then processed by a Northern NS-623 8192 analog to digital converter (ADC NIM module; Northern, a subsidiary of Middleton, Wisconsin, U.S.A.) and then by a Canberra multichannel analyzer computer board System 100 Version 2.1 (© 1987; ibid). Only one electrode signal could be processed at a time so that two separate amplifier circuits (one for each electrode) fed into the ADC NIM module. The V1 circuit was used for the experiments in this thesis.

### 7.4 Description of the Isobar Separator for Anions

Figure 7-4 shows a schematic representation of the ISA components. The ISA consisted of five basic regions:

1. a deceleration region which used large electrodes to reduce the ion energy from the ion source exit energy to approximately 4 keV,
2. a second deceleration region using radio-frequency quadrupoles (RFQ)s and aperture lenses to reduce the energy to below $\Delta V_{SISA}$. This also served as a differential pumping region,
3. the collision cell, which contained an RFQ as well as gradient electrodes to maintain the axial momentum of the cooled anions, housed within a stainless steel sleeve,
4. a drift and differential pumping region similar in design to region 2 with modest ion reacceleration, and
5. a final reacceleration region with acceleration potential $V_{ISA}$ (close to the original ion acceleration potential from the ion source, $V_S$, see Eq 7.1; this is the inverse of region 1).

Figure 7-4: Schematic Representation of the ISA Through 1 Plane

Cy – cylinder; Co – cone; GR – gradient bar; L – lens aperture; RFQ – radio-frequency quadrupole. Different cells were used, the initial without GR. Variously, $f = 2.3 – 2.6$ MHz was used with $0 \leq V_{pp} \leq 2000$ V; 2 RFQ sets shared a single rf oscillator, see Figure 7-5 for dimensions and Figure 4-1 for definitions. Ions underwent deceleration initially from a cylinder-cone pair of electrostatic lenses and then by DC voltages applied to RFQs and lens apertures, $\Delta V_{ISAS}$ is the difference between the ion source ($V_S$) and ISA ($V_{ISA}$) deck voltages (Eq 7.1). The reacceleration region was the inverse of the deceleration region and was followed by a 500 mm ‘dead zone’. Pressure in this region was relatively high when gas was used in the ISA but was located directly above the ISA chamber cryo-pump so that pressure would have been lower than at the ISA entrance. Not shown are the gas leak inlet port on the collision cell for introduction of gas and the outlet port for direct measurement of cell pressure.

The RFQs were operated between $2.3 – 2.5$ MHz (adjustable) and not only guided the ion beam at low energy but also reduced losses due to space charge effects. Each lens and RFQ had a
separate DC power supply; the RFQ DC voltage was the same on all rods so the RFQ did not act as a mass filter (see section 4.1). The outer sleeve of the reaction cell (ID \( \phi 68 \) mm) was connected to the RFQ DC voltage. Two RFQ rod sets shared 1 rf power supply so that both had the same \( q_2 \) (Eq 4.19). In the cell, a gradient electrode was located between each pair of RFQ rods. Each gradient electrode was tapered so that a voltage applied to them would result in a small gradient \( \leq 10 \) mV/cm along the axis of the cell to help ions maintain an average small forward momentum during collisions with gas. Dimensions are given in Figure 7-5 and an electrical schematic in Figure 7-6.

**Figure 7-5: Collision Cell Quadrupole Rod and Gradient Bar Offset Dimensions**

<table>
<thead>
<tr>
<th></th>
<th>Injection (mm) ( \pm 0.02 )</th>
<th>Exit (mm) ( \pm 0.02 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>15.20</td>
<td>21.35</td>
</tr>
<tr>
<td>B</td>
<td>15.50</td>
<td>21.35</td>
</tr>
<tr>
<td>C</td>
<td>13.81</td>
<td>13.81</td>
</tr>
<tr>
<td>D</td>
<td>13.81</td>
<td>13.81</td>
</tr>
</tbody>
</table>

Gradient bars are blue and quadrupole rods are grey. The RFQ length was 152.5 \( \pm 0.5 \) mm. Rod dimensions and lengths were the same for RFQ1, 2, 3 and 4 (Figure 7-4).

Gas was introduced to the collision cell through 2.1 mm ID stainless steel tubing that led from externally mounted gas cylinders, through a Varian model 951-5106 variable leak valve (Varian Inc., Palo Alta, California, U.S.A.) to the vacuum box. From the vacuum interface, 3.2 mm ID Teflon tubing (Upchurch Scientific, Scivex, Oak Harbor, Washington, U.S.A.) was used. Silver wool was inserted in the NO\(_2\) gas feed line in order to reduce contaminant SO\(_x\) compounds. A second port using 6.4 mm ID Teflon and 7.8 mm ID stainless steel tubing connected the cell to a Baratron 626A pressure gauge (MKS Instruments, Andover, Massachusetts, U.S.A.) mounted externally to the chamber for direct reading of the collision cell pressure. The deceleration and
acceleration regions were designed as quasi-Einzel lenses with the final electrode modelled after the ion source target acceleration electrode Pierce geometry. There was a 500 mm ‘dead zone’ following the exit ground electrode that was shielded with a perforated metal jacket maintained at ground potential. This region would have been at relatively high pressure (on the order of the chamber pressure) when gas was used. In such a region, unwanted ion loss or production may result from high energy ion-gas interactions. A magnet was placed on the ISA chamber lid midway along this section for electron suppression.

**Figure 7-6: rf Quadrupole Rod Electrical Circuit Schematic**

Power supplies were located on a rack above the ISA and referenced to the deck voltage. Control was through a remote computer connected through a fibre-optic cable. Rod rf A and B were $\pi$ out of phase sinusoidal signals with $0 \leq |V_{rf}| \leq 2000$ V. Two rod-sets shared the same $V_{rf}$ and each individual quadrupole unit could have an additional static (DC) voltage offset $-200 \leq V_{dc} \leq 200$ V (same voltage on all 4 rods).

Tuning the settings of the ISA as the reaction gas pressure was varied was necessary to maintain optimum transmission and was not found to depend on the mass of the ions significantly within a range of roughly $\pm 10$ amu from the tuning mass for $m < 60$ amu. Tuning was done sequentially, first optimizing the beam into FC2, then through the cell with the steerers
and lenses before the ISA chamber, then by adjusting the deceleration and acceleration sections, then the RFQ’s and lenses, and then repeating the process.

As will be discussed in chapter 8, the φ3 mm apertures appear to have been restrictive for the ion beams and, given the number of parameters to be varied, tuning was rather tedious and laborious. Achieving consistent and optimum transmission required tuning for each experiment separately and consumed a large portion of the experimental time. Increasing the aperture radii would improve the situation as long as the chamber ambient pressure could be moderated at higher collision cell pressures. For higher pressure measurements when anions are cooled, a smaller cell exit aperture would likely not be too restrictive. Lower pressure measurements, however, would be easier with larger apertures. Use of a longer cell would allow for operation at lower pressure as the increased interaction region could facilitate an equivalent average number of anion–gas collisions as occur in a shorter cell at higher pressure. The collision rate, of course, would be reduced as the average ion path-length between collisions would be increased (Eq 6.29).

### 7.5 Sputter Target Material, Cs and Gas Manufacturer Information

**Ion Source:**

<table>
<thead>
<tr>
<th>Cs (sputter source)</th>
<th>Cabot Corp., Revere, Pennsylvania, U.S.A.</th>
</tr>
</thead>
</table>

**Gases used in ISA:**

<table>
<thead>
<tr>
<th>Ar (PP 4.8)</th>
<th>GP 529325</th>
<th>Praxair Products Canada Inc., Mississauga, Ontario, Canada</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>GP 529205</td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>GP 529005</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td></td>
<td>Matheson of Canada Ltd., Whitby, Ontario, Canada</td>
</tr>
<tr>
<td>N₂O</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Target powders were pressed into 7 mm long, φ6 mm cylindrical Al target holders with a φ2 mm hole bored through the centre along the length. Back-plugs were made of Cu. Manufacturer information is given for target powder materials on the next page.
### Powders Used to Make Sputter Targets:

<table>
<thead>
<tr>
<th>Formula</th>
<th>Lot</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag (2.0 – 3.5 μm)</td>
<td>F15G - 00786</td>
<td>Alfa Aesar – A Johnson Matthey Company, Danvers, Massachusetts, U.S.A.</td>
</tr>
<tr>
<td>BaCl₂·2H₂O</td>
<td>1-0970</td>
<td>J.T. Baker Chemical Company, Phillipsburg, New Jersey, U.S.A.</td>
</tr>
<tr>
<td>CuSO₄</td>
<td></td>
<td>manufacturer details unknown</td>
</tr>
<tr>
<td>KCl</td>
<td>732115</td>
<td>Fisher Scientific Company (see CaF₂)</td>
</tr>
<tr>
<td>NaCl</td>
<td>5010</td>
<td>Merck, Québec, Canada</td>
</tr>
<tr>
<td>NaCl + S</td>
<td></td>
<td>The sulphur spike is unknown, but data taken with S⁻ and Cl⁻ from this material was consistent with all other S⁻ and Cl⁻ data</td>
</tr>
<tr>
<td>Nb (60 mesh)</td>
<td>061981</td>
<td>Alfa Aesar (see Ag)</td>
</tr>
<tr>
<td>PbF₂</td>
<td>2694510</td>
<td>The British Drug Houses Ltd., Poole, England</td>
</tr>
<tr>
<td>SrF₂</td>
<td>596967</td>
<td>Johnson Matthey – Materials Technology U.K., Hertz, England</td>
</tr>
<tr>
<td>YF₃</td>
<td></td>
<td>manufacturer details unknown</td>
</tr>
<tr>
<td>ZnO</td>
<td></td>
<td>manufacturer details unknown</td>
</tr>
<tr>
<td>ZrF₄</td>
<td></td>
<td>manufacturer details unknown</td>
</tr>
</tbody>
</table>

#### 7.5.1 NO₂/N₂O₄ Equilibrium Ratio

In the gas phase, NO₂ exists at equilibrium with the dimer N₂O₄. Dupé (2004 p. 88 - 89) addresses the concern for room temperature and gives the following formula for pressure, P ≪ atmosphere (760 Torr):

\[
\frac{x^2}{(P_0 - x)} = 0.135
\]

Here, x represents the fugacity and determines \( P(\text{NO}_2)/(1 \text{ atmosphere}) \), and \( P_0 \) is the ratio of the gas pressure to 1 atmosphere of pressure. A convenient expressions for calculations in this thesis is \( P_0 = (P \text{ [mTorr]})/(7.6 \times 10^5 \text{ [mTorr]}) \). Solving for x using the quadratic equation gives,

\[
x = -0.0675 \pm \sqrt{4.55625 \times 10^{-3} - 0.135 \cdot P_0}.
\]

At a pressure of \( P = 1 \text{ mTorr} \), \( P_0 = 1 / (7.6 \times 10^5) \).

Substituting this in for x (using the positive root) and multiplying the result by 760 Torr (1 atmosphere), at \( P = 1 \text{ mTorr} \) the mixture of NO₂/N₂O₄ (at 298 K) should be > 99.999% NO₂. At 6 mTorr, the mixture should be > 99.994% NO₂.
7.6 Typical Settings

Refer to Figure 7-1 for positions and symbol meanings. Faraday cup suppressions are given in the figure. Targets were sputtered by 4 keV Cs⁺ and typically accelerated to 20 keV at the ion source.

Table 7.2: Typical Slit Openings (mm)

<table>
<thead>
<tr>
<th>FC1</th>
<th>T 10</th>
<th>B 10</th>
<th>N 10</th>
<th>S 10</th>
<th>FC4</th>
<th>T 5</th>
<th>B 5</th>
<th>E 3</th>
<th>W 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>FC5</td>
<td>T 1.5</td>
<td>B 1.5</td>
<td>E 2</td>
<td>W 2</td>
<td>FC6</td>
<td>T N/A</td>
<td>B N/A</td>
<td>N 2.75</td>
<td>S 1.75</td>
</tr>
</tbody>
</table>

Table 7.3: Typical AMS Settings for X⁻ → X⁺³

| Accelerator terminal voltage (VT) | 1.7103 MV (dial set to 17500) |
| Stripping canal Ar                | 1.5 μg/cm²                      |
| LEP / HEP                        | 1.7 / 2.0 x 10⁻⁷ Torr           |
| Ionization detector voltages [V, Figure 7-3] | V1 = 450 ; V2 = 400 ; V3 = 250 |
| Ionization detector C₄H₁₀ pressure | usually 18 Torr (ranged from 15 – 20 Torr) |

7.7 Stripping Yield vs. Accelerator Terminal Voltage Correction

Stripping yield to a particular charge state in the Ar column at the tandem accelerator high voltage terminal depends on energy and gas pressure. A useful reference for voltage selection is Wittkower and Betz (1973). Over the course of this PhD many measurements were made by stripping X⁻ → X⁺³ (X represents an element such as Cl, S, Si) because the atomic mass, m, divided by q (= +3) resulted in a non-integral number, reducing measurement background from other fragments with integer multiples of m/q (see section 2.2). At q = +3 it has also been found that molecular anion dissociation, at least for smaller molecules composed of the lighter elements, is very efficient (Lee et al. 1984, Lee 1988).

Relative abundances of anions containing X from interactions X⁻ + gas → XY⁻ where Y itself may be one or several atoms, were also sought. Maintaining the same X⁺³ stripping yield when XY⁻ was injected into the stripper instead of X⁻ would have required raising the terminal voltage, VT, since the energy available for stripping to X⁺³ is proportional to the mass ratio m/M.
(m is the mass of X, M of the molecule). This was limited by the available range of $V_T$ in many cases and also increased analysis time as it required a change in settings of the magnet and electric analyzers following the accelerator. Similarly, higher gas pressure could have increased yields but can also lead to more scattering and ion losses in the accelerator acceleration tubes, and the time needed for pressure equilibration made this impractical for most measurements.

In several cases it was much more practical to simply scan $V_T$ with the magnet and electric analyzers set for a particular $m/q$ and $K_0/q$. With $B$ the magnetic field, $E$ the electric field of the electric analyzer, $\rho$ the deflection radius, $q^-$ and $M$ the anion charge and mass, $q^+$ and $m$ the charge and mass of the positive fragment, and $V_T$ the terminal voltage (see Table 2.1),

$$B\rho \propto \sqrt{m \left( q^+ + \frac{m}{M} q^- \right) V_T}$$

$$E\rho \propto \left( q^+ + \frac{m}{M} q^- \right) V_T$$

If ions were injected into the accelerator with different initial kinetic energies then these equations would need to be modified slightly. Using initial settings for a known fragment and parent for calibration with Eq 7.3 and 7.4, the parent $M$ at different $V_T$ could then be determined by the ratio of the different $V_T$ used. However, ‘scanning the terminal ($V_T$ scan)’ measurements do not maintain constant stripping energy. Rather, the stripping energy available to $m$ decreases with $M$ if $B\rho$, $E\rho$, $m$, $q^+$ and $q^-$ are constant.

In order to correct for stripping yield decreases, a steady beam of $^{32}\text{S}^-$ was injected with typical AMS settings (section 7.6), stripper pressure was held constant to imitate experimental conditions, and the $^{32}\text{S}^{+3}$ current at FC7 was recorded for four values of $V_T$. Unfortunately, measurements were limited to four values because one of the components of the AMS system failed and, after reparation, time on the system was too limited. IsoTrace Laboratory lost operational funding from University of Toronto and had to be closed for a little over 6 months. Funding to re-open was made available by University of Ottawa, but by then funding for doctoral work was too limited to continue with calibration measurements. Future measurements should also include confirmation that $\text{S}^{+3}$ stripping yields from molecules, such as $\text{SO}^-$ and $\text{NSO}_2^-$, are similar.

The data span 1 – 1.7 MV and show a relative yield of 22% at the lowest voltage compared to the highest. Given their proximity in the periodic table, $\text{S}^-$ and $\text{Cl}^-$ stripping yields
in Ar should be similar. Wittkower and Betz (1973, p. 139) give the yield of Cl$^-$ → Cl$^{+3}$ in Ar at 1 MV as 18% and at 2 MV as 35.9%, for a 50% relative yield. Kiisk et al. (2004, fig. 8) give the yield of Cl$^-$ → Cl$^{+3}$ in Ar at 2.2 MV as 39% and 1.6 MV as 30%, for a relative yield of 75%.

**Figure 7-7: Cl$^-$ → Cl$^{+3}$ Equilibrium State Stripping Yields from References and Comparison to Measured $^{32}$S$^-$ → $^{32}$S$^{+3}$ Relative Intensities**

Cl$^-$ → Cl$^{+3}$ absolute stripping yields from two references plot well linearly over 1 – 2 MeV. Measured S$^-$ → S$^{+3}$ intensities were converted to absolute stripping yields using the linear fit to the Cl$^{+3}$ data (see text) to compare the data sets. Optimum Ar stripping pressures were not sought for the S$^{+3}$ data and tuning was constant over the full range of acceleration voltages used, $V_T$. Considering that the pressures were adjusted for the equilibrium state stripping yields from the references, the data plot remarkably well against each other.

The Cl$^{+3}$ yield data from the references are shown in Figure 7-7, which also shows a comparison with the present $^{32}$S$^{+3}$ calibration measurements. A linear fit was calculated for the Cl$^{+3}$ data from 1 – 2 MeV using the least squares method (details can be found in Bevington 1969). Plotting statistics are given in the figure and from the correlation coefficient (0.9953) and standard deviation (0.87595) it can be seen that the data fit was very good.
$S^{+3}$ measurement currents at $\text{FC7}$ were normalized to the $V_T = 1.7$ MV data where tuning was optimized. Using the $\text{Cl}^{+3}$ linear fit equation (given in the figure), a theoretical $^{32}S^{+3}$ absolute stripping yield at $1.7$ MV was calculated to be $31.5\%$. With $I_J$ representing the measured current at $V_T = J$ MV, theoretical yields, $Y_{th}$, for the other points were calculated using $Y_{th} = (I_J/I_{1.7}) \times 31.5\%$. The data plot remarkably well against each other, especially considering that the references present equilibrium measurements with pressure adjustments made to determine precise $q = +3$ populations.

A linear fit was then calculated for the measured $^{32}S^{+3}$ data by the least squares method, with data normalized to the $^{32}S^{+3}$ current at $1.7$ MV. However, the $^{32}S^{+3}$ data showed a non-linear trend so a second order polynomial fit was also computed using Origin 7.5 and appears to fit the data much better. This is probably because the stripping pressure and tuning conditions were constant over the entire range of $V_T$ and, strictly speaking, the data should not be exactly linear. However, with only 4 data points it is quite difficult to determine the true nature of the data linearity. Curves and data are presented in Figure 7-8.

Between $0.95$ MV and $1.85$ MV the linear and non-linear corrections do not differ by more than $5\%$, and from $1$ MV to $1.7$ MV they are within $2.5\%$. These are the ranges used during the vast majority of experiments so that choice of either correction is rather inconsequential given the size of other experimental uncertainties (eg. see sections 9.2 and 10.1). Because tuning and pressure conditions make it very plausible, the non-linear equation will be used and a note will be made when the two corrections would differ by more that $5\%$.

The equation of fit can be used to correct data presented in this thesis for relative stripping yields (not absolute) to $q = +3$ over a limited range of isotopes for typical ISA experimental conditions. For a given $V_T$, a ‘stripping voltage’, $V_{TS}$ can be calculated as:

$$V_{TS} = \left(\frac{m}{M}\right) V_T$$

where $m$ is the mass of the fragment and $M$ is the mass of the parent molecule. Then, $V_{TS}$ can be used with the fit equation to determine a scaling factor for the measured peak intensity.
Figure 7-8: $^{32}\text{S}^- \rightarrow ^{32}\text{S}^{+3}$ Stripping Data and Curve Fits for Stripping Yield Corrections

In the legend, $R$ is the correlation coefficient and $SD$ is the standard deviation.

The Ar stripper pressure and AMS tuning conditions were constant over the full range of $V_T$ which could explain a non-linear nature to the stripping yield, as opposed to the trend from equilibrium state stripping for Cl$^-$ to Cl$^{+3}$ in Figure 7-7. Between 0.95 MV and 1.85 MV the two fits differ by < 5%, and from 1 MV to 1.7 MV (typical experimental ranges) they are almost in agreement. Because tuning and pressure conditions make it very plausible, the non-linear equation will be used for corrections using $V_{TS}$ (Eq 7.5) for $x$. In cases where the linear and non-linear corrections would differ by more that 5%, a note will be made.
8 ISA Vacuum Transmission and $q_2$ Focussing

Transmission is rather important in AMS because the isotopes under study are at extremely trace levels. Losses during beam transport increase counting times, lower counting statistics and can negate the possibility of the lowest level measurements. Data uncertainty increases and measurement reliability, precision, and accuracy are all compromised when the losses are not well understood or vary unpredictably with time. Maintenance of stable currents and high transmission are key requirements for any isobar separation instrument added to an AMS system.

The Isobar Separator for Anions has many different components and high transmission through the apertures required careful tuning. Tuning was very sensitive to the lens and quadrupole rf voltage settings, making it difficult at times to obtain consistent data and placing large time demands on the operator when highly precise measurements are needed. This is currently being considered and the system design modified. This section examines some areas of beam loss and discusses some possible design improvements.

In the following, $V_{ISA}$, $V_s$ and $\Delta V_{ISAS}$ are as defined in Eq 7.1, notations from Figure 7-1 and Figure 7-4 are used and the instruments described in chapter 7 are referenced by name only. Data were taken for vacuum transmission through the ISA using both collision cells (with and without GR) and with various aperture diameters (Figure 7-4).

8.1.1 Transmission vs. Transverse Ion Kinetic Energy

Figure 8-1 shows the effect of the rf quadrupoles and DC lenses on ion transmission. A beam of $^{12}C_3^-$ was produced from a graphite target (2.6 $\mu$A at FC1; FC1 slits T/B/N/S 10 mm) with $V_s = -20.444$ kV and monitored at FC2 after analysis by magnet 1. As a minor digression, a note on why this anion was chosen may be in order.

These represent some of the first data taken, long before any work with Cl$^-$ or S$^-$ had been started. Typically, tuning for $^{14}$C measurements was done (at IsoTrace) with graphite targets, which were available in abundance and seemed reasonable to use for these early measurements. $^{12}C_3^-$ was used because it has mass 36 amu and the first major series of experiments planned for the ISA were meant to look at $^{36}$Cl$^-$ analysis capabilities. As discussed in more detail in section 10.3.6, the energy spread of molecular anions produced from AMS Cs$^+$ sputter sources has been found to be very different than that of most atomic anions. Typically,
the larger the molecular anion, the narrower the anion beam energy spread. In some cases the low energy ‘tail’ can be larger than that of atomic anions, but the high energy ‘tail’ is almost always found to be much lower in magnitude and may be non-existent in many cases. These results were not contrasted with a beam of atomic anions.

Voltage readings were taken with the Fluke meter and probe. ISA settings were optimized with $\Delta V_{\text{SISA}} = 1 \text{ V}$ (offset between ion source and ISA deck voltages, Eq 7.1) for transmission to FC3, where all transmission (FC2 to FC3) measurements were made. System pressures and ISA settings are given in the figure.

The goal was to assess how transmission was affected by the rf quadrupoles and DC lenses in the ISA. Four conditions were tested (DC refers to the ISA Cy, Co, L and RFQ DC voltages): a) neither rf nor DC voltages applied b) only DC applied, no rf c) only rf, applied, no DC, and d) rf and DC voltages all applied. Under each scenario, $V_{\text{ISA}}$ was scanned from 0 to $V_s$ and the beam was focussed using the elements before the ISA chamber at each measurement. Currents at FC2 are given in the figure and varied between 120 – 330 pA. For conditions a) and c) the current drifted very slowly and steadily over the run, not affecting the results (all data normalized to FC2 current).

With all of the ISA voltages set to 0 V (off), a), there is a focussing peak at $\Delta V_{\text{SISA}} = 6.147 \text{ kV}$ after which the current drops quickly. There appears to have been a quasi-focal point from the fringing fields of the chamber. This peak represented less than 70% transmission, lower than that achieved with the ISA operating as discussed below.

With the ISA DC voltages on without the rf, b), there are two focussing peaks. The second peak and the offset between the first peak and that in condition a) arise from the ISA lenses, especially in the deceleration and acceleration regions.

With only the rf applied, condition c), the second focussing peak disappears as the ISA focussing acceleration and deceleration regions are not active. Without focussing into and out of the rf quadrupole region of the ISA there is little transmission, even at low ion energy ($\Delta V_{\text{SISA}}$), despite the rf trapping potential.

With all of the ISA voltages active > 80% transmission is achieved for $\Delta V_{\text{SISA}} < 100 \text{ V}$, and even as low as $\Delta V_{\text{SISA}} = 13 \text{ V}$ the transmission is 80%. The transmission is ‘choppy’, rising and falling over the energy scan, but the pattern is readily understandable from the discussion in section 5.4.3.2, Figure 5-27 and Figure 5-28.
Figure 8-1: Transmission vs. ISA Deck Voltage with and without ISA rf and DC

RF refers to both rf power supplies and DC to the voltages applied to the ISA elements. A 20.444 keV $^{12}\text{C}_3^-$ beam was monitored with FC2 (current is given in legend in brackets, the drift for 2 runs was slow and steady, not affecting the results). Transmission from FC2 to FC3 was observed with ISA elements variously turned off or on while scanning $V_{ISA}$ from 0 to $V_S$. At each measurement the beam was tuned using the elements before the ISA chamber, ISA settings were not adjusted. This meant $q_2$ and $T_0(\omega)$ (Eq 4.19, Eq 5.13) were constant as $Ln_{rf}$ (Eq 4.28) varied. The transmission peaks with all ISA voltages applied correspond to half-integer values of $Ln_{rf} / T_0(\omega)$ within the collision cell, indicating that eliminating or widening the cell apertures could greatly enhance transmission.
No attempt was made to increase transmission by varying the rf or DC voltages of the ISA during the scan. With $V_{pp} = 500\, \text{V}$, $m = 36\, \text{amu}$, $r_0 = 6.905\, \text{mm}$, $q = 1$ and $f = 2.6\, \text{MHz}$, the stability parameter for these ions is $q_2 = 0.211$ (Eq 4.19), well within the limits of the low-$q_2$ approximations discussed in chapters 4 and 5. Since there was no ISA tuning, $q_2$ was constant as was the relative period of rf trajectory $T_0(\omega) = 13.43$ (Eq 5.13). Using Eq 4.28 to calculate $L_{\text{rf}}$, the length of time relative to the rf frequency spent in the collision cell (eg. between the 2 sets of smallest, 2 mm, apertures) at each energy value can be calculated using 150 mm for length.

The value $\frac{L_{\text{rf}}}{T_0(\omega)}$ (as used in Figure 5-27 and Figure 5-28) can then be determined, describing how many periods of ion motion can be completed for the given ion residence time in the RFQ. Values are given in brackets in Figure 8-1. Transmission minima are at integer values (1, 2, 3) while maxima are at half-integer values (1.5, 2.5, 3.5). This indicates that elimination or widening of the small apertures would result in much more even transmission over the scan without the need to constantly tune the ISA settings, with > 80% transmission over a broad range of energies possible.

8.1.2 Transmission vs. RF2 $V_{pp}$ at Fixed $\Delta V_{\text{ISAS}}$ – ‘$q_2$ Focussing’

Ideal ion transmission in an rf quadrupole instrument is flat-topped for $0 < q_2 < 0.908$ (section 4.1.1) when the applied rf voltage, $V_{pp}$, is scanned. Initial radial ion energy, position and several other factors can result in a reduced $q_2$ transmission range (chapter 5). Apertures can cause ‘jagged’, ‘saw-toothed’, non-flat-topped transmission (theoretical discussion and simulations in section 5.4.3, experimental evidence in section 8.1.1). The aperture effect was not well understood during the initial measurements with the ISA, however some of the early data show that the collision cell apertures contribute to tuning difficulties and transmission losses.

In the initial cell, there was an 8 mm aperture directly following (~ 0.5 mm) the collision cell 2 mm exit aperture, and another 4 mm aperture (Co2) 150 mm downstream. With all of the lenses set to 0 V, when the ion beam was well focussed through the 2 mm cell entrance aperture then any transmission losses were dominated by the collision cell exit apertures during an RF2 voltage scan. While the deceleration and acceleration regions are needed in order to have any reasonable transmission through the ISA (see section 8.1.1 and Figure 7-4), the other DC voltages are not needed when large absolute transmission is not needed.
Figure 8-2: Transmission vs. ISA RF2 $V_{pp}$ – ‘$q_2$ Focusing’ Peaks

An 8 nA (FC2) beam of $^{32}\text{S}^-$ was generated with $V_s = -15.736$ kV. With $\Delta V_{\text{ISA}} = 10.0 \pm 0.3$ V, the ISA transmission profile FC2 to FC3 was monitored while varying RF2 with all DC voltages set to 0 V except in the deceleration and acceleration regions after transmission. The $q_2$ (Eq 4.19) values were calculated from $V_{pp}$, and $\ln r_f$ and $T_0(\omega)$ are given by Eq 4.28 and Eq 5.13 respectively. The transmission peaks are well described by ‘$q_2$ focussing’ at the small exit aperture of the collision cell.

Pressure x $10^{-7}$ Torr:
- FC1 1.4; ISA chamber 2.7; AA 0.63;
- Slits FC1 T/B/N/S 10mm

<table>
<thead>
<tr>
<th>RF2 scan</th>
<th>3500</th>
<th>220</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>1800</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>560</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

$\phi$ (mm) 4 8 8 2 2 8 4

Cy1 Co1 RFQ1 DC L1 RFQ2 DC Supply 1 L3 RFQ3 DC L5 RFQ4 DC Supply 2 Co2 Cy2

(RF $V_{pp}$ else V)
Using $V_s = -15.736$ kV, a beam of $^{32}\text{S}^-$ was produced from an Nb + (NaCl + S) target (3:1 vol, FC1 slits T/B/N/S 10 mm) and monitored at FC2 (= 8 nA) after analysis by magnet 1. Voltage readings were taken with the Fluke meter and probe and $\Delta V_{\text{SISA}}$ was set to $10.0 \pm 0.3$ V. After ISA settings were optimized for FC2 to FC3 transmission, the DC settings from Co1 to Co2 were set to 0 V and RF1 was left at the optimum setting so that rf only transmission through the collision cell could be studied. The RF2 $V_{pp}$ was scanned and FC3 current readings recorded.

Results are shown in Figure 8-2. The $q_2$ values (Eq 4.19) were calculated from $V_{pp}$ using $q = 1$, $m = 32$, $r_0 = 6.905$ mm, $f = 2.6$ MHz, and are plotted on the bottom axis of the top panel and the top axis of the bottom panel. The top panel top axis shows the $V_{pp}$ for each measurement. The bottom panel shows $L_{\text{nf}} / T_0(\omega)$ (Eq 4.28 and 5.15, discussed in sections 5.4.3 and 8.1.1) calculated with $l = 150$ mm, $K_z = 10$ eV and the values just given. This value represents the number of rf trajectory oscillations an ion undergoes on average within a length defined by $L_{\text{nf}}$.

Ion transmission begins at $q_2 = 0.047$ where $V^*(r_0) = 0.6$ eV and $V^*(r = 1$ mm) = 0.01 eV suggesting that ion radial energy $K_r \geq 0.01$ eV ($V^*$ is the effective potential, discussed in section 4.1.2, given by Eq 4.40, useful for low $q_2 < 0.4$ as demonstrated in section 5.3.2). By $q_2 = 0.3$ where $V^*(r = 1$ mm) = 0.50 eV, the 1% transmission maximum value has been reached suggesting that $K_r > 0.5$ eV for the majority of the ions. A sharp drop in transmission begins at $q_2 = 0.711$, and this is where trajectory amplitudes cease to decrease with rising $q_2$ and begin to increase (eg. as in Figure 5-2 and Figure 5-9). This all suggests that ion radial energy is rather large on average and ion trajectory amplitudes exceed 2 mm.

The bottom panel shows that the curve structure fits the model of $q_2$ focussing (section 5.4.3.2) very well. When the average number of rf cycles that an ion spends in the collision cell ($L_{\text{nf}}$) is a half-integer multiple of the average rf oscillation period for a given $q_2$ value ($T_0(\omega)$), $L_{\text{nf}} = k/2 T_0(\omega)$ for $k$ an integer, there is always a maximum in transmission. The only exceptions are at $k = 1$ where there is no transmission, $k = 4$ where there is a plateau and $k = 12$ where transmission is rising rapidly and not many data points were taken to reveal any structure. That is, when the oscillation period has a node at the exit of the cell, more ions pass through the aperture. Conversely, $L_{\text{nf}} = k/4 T_0(\omega)$ for $k$ an odd integer represents an anti-node at the exit aperture, and the transmission generally has a local minimum. Some offset from exact values can be expected because of focussing effects at the entrance aperture of the cell (fringing fields) and before (deceleration region and passage between RFQ1, L1 and RFQ2). As expected, the approximation gets worse for $q_2 > 0.4$. 
Not only do the apertures have the effect of limiting the radial energy spread that can be transmitted but they also cause a structure to the transmission curve, especially for low q2, with several rather sharp tuning positions.

### 8.1.3 Large Aperture Transmission

#### Table 8.1: Transmission (FC2 to FC3) Results with L3 and L4 Removed

<table>
<thead>
<tr>
<th>Ion</th>
<th>(\Delta V_{\text{ISAS}}) (V)</th>
<th>(V_s) (kV)</th>
<th>FC1 (μA)</th>
<th>ISA Settings</th>
<th>FC2 (± 2%)</th>
<th>FC3 (± 2%)</th>
<th>FC3/FC2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{35}\text{Cl})</td>
<td>10.1 ± 0.3</td>
<td>–20.6315</td>
<td>10.5</td>
<td>A</td>
<td>28 nA</td>
<td>28 nA</td>
<td>100</td>
</tr>
<tr>
<td>(^{35}\text{Cl})</td>
<td>1.50 ± 0.04</td>
<td>–20.6285</td>
<td>4.7</td>
<td>B</td>
<td>19 nA</td>
<td>19 nA</td>
<td>100</td>
</tr>
<tr>
<td>(^{19}\text{F}^-)</td>
<td>1.09 ± 0.03</td>
<td>–20.6303</td>
<td>2.2</td>
<td>C</td>
<td>1.20 μA</td>
<td>1.05 μA</td>
<td>87.5</td>
</tr>
</tbody>
</table>

For ISA settings and apertures refer to Table 8.2. Slits at FC1: T/B/N/S 10 mm. With reference to the ISA Settings column, pressures at (FC1, ISA Chamber, AA; x 10\(^{-7}\) Torr): A (4.5, 24, 7.8), B (5.2, 5.5, 1.8), C (4.0, 9.0, 4.1).

Target material: KCl + CaF\(_2\) + PbF\(_2\). Voltages measured using resistor chain and Keithley multimeter.

#### Table 8.2: ISA Settings for Transmission Studies with L3 and L4 Removed

<table>
<thead>
<tr>
<th>Cy1</th>
<th>Co1</th>
<th>RFQ1</th>
<th>DC</th>
<th>Supply 1 RF</th>
<th>L1</th>
<th>RFQ2</th>
<th>DC</th>
<th>Supply 2 RF</th>
<th>L2</th>
<th>RFQ3</th>
<th>DC</th>
<th>GR</th>
<th>L5</th>
<th>RFQ4</th>
<th>DC</th>
<th>Supply 2 RF</th>
<th>Co2</th>
<th>Cy2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>RF Vpp</td>
<td>else V</td>
<td></td>
<td>4</td>
<td>8</td>
<td>8</td>
<td></td>
<td>8</td>
<td>280</td>
<td>0</td>
<td></td>
<td>3</td>
<td>2100</td>
<td>2050</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A (10.1 eV 28 nA) | 1900 | 1400 | 26 | 0 | 15 | 0 | 4 | 0 | 3 | 2100 | 2050 | 280 | 0 | 350 |

B (1.5 eV 19 nA) | 1900 | 2200 | 40 | 15 | 20 | 0 | 20 | 0 | 0 | 2100 | 2050 | 280 | 0 | 350 |

C (1.1 eV 1.20 μA) | 1900 | 2400 | 30 | 10 | 30 | 5 | 20 | 15 | 100 | 2100 | 2050 | 250 | 0 | 350 |

These settings are for the FC2 to FC3 transmission test results given in Table 8.1.
Table 8.3: Transmission (FC2 to FC3) Results with L2 = L3 = φ3 mm and L4 Removed

<table>
<thead>
<tr>
<th>Ion</th>
<th>ΔV_{\text{ISAS}} (V)</th>
<th>V_s (kV)</th>
<th>FC1 (μA)</th>
<th>ISA Settings</th>
<th>FC2 (± 2%)</th>
<th>FC3 (± 2%)</th>
<th>FC3/FC2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35Cl</td>
<td>10.4 ± 0.3</td>
<td>-20.7018</td>
<td>1.95</td>
<td>D</td>
<td>10 nA</td>
<td>10 nA</td>
<td>100</td>
</tr>
<tr>
<td>35Cl</td>
<td>10.4 ± 0.3</td>
<td>-20.7018</td>
<td>8.6</td>
<td>E</td>
<td>92 nA</td>
<td>86 nA</td>
<td>93.5</td>
</tr>
<tr>
<td>35Cl</td>
<td>1.00 ± 0.03</td>
<td>-20.7018</td>
<td>1.95</td>
<td>F</td>
<td>850 pA</td>
<td>740 pA</td>
<td>87.1</td>
</tr>
</tbody>
</table>

For ISA settings and apertures refer to Table 8.4. Slits at FC1: T/B/N/S 10 mm. Pressures for all measurements at (FC1, ISA Chamber, AA; x 10^{-7} Torr): (4.3, 4.1, 1.2). Target material: KCl + CaF₂ + PbF₂. Voltages measured using resistor chain and Keithley multimeter.

Table 8.4: ISA Settings for Transmission Studies with L2 = L3 = φ3 mm and L4 Removed

<table>
<thead>
<tr>
<th>Cy1</th>
<th>Co1</th>
<th>RFQ1 GR</th>
<th>L1 GR</th>
<th>RFQ2 GR</th>
<th>L2 GR</th>
<th>RFQ3 GR</th>
<th>L3 GR</th>
<th>RFQ4 GR</th>
<th>L5 GR</th>
<th>Cy2</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1640</td>
<td>4000</td>
<td>26</td>
<td>0</td>
<td>0</td>
<td>110</td>
<td>0</td>
<td>20</td>
<td>40</td>
<td>2000</td>
</tr>
<tr>
<td>(10.4 eV 10 nA)</td>
<td>147</td>
<td>7</td>
<td>0</td>
<td>420</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>1660</td>
<td>3800</td>
<td>32</td>
<td>1</td>
<td>8</td>
<td>150</td>
<td>25</td>
<td>50</td>
<td>50</td>
<td>4000</td>
</tr>
<tr>
<td>(10.4 eV 92 nA)</td>
<td>197</td>
<td>5</td>
<td>0</td>
<td>800</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1640</td>
<td>4000</td>
<td>32</td>
<td>1</td>
<td>8</td>
<td>150</td>
<td>0</td>
<td>40</td>
<td>50</td>
<td>4000</td>
</tr>
<tr>
<td>(1.0 eV 850 pA)</td>
<td>160</td>
<td>10</td>
<td>0</td>
<td>420</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

These settings are for the FC2 to FC3 transmission test results given in Table 8.3.

When the first collision cell was exchanged for a collision cell with gradient bars, the φ2 mm apertures at L3 and L4 were removed in order to test transmission with only the φ8 mm apertures at the entrance and exit of the collision cell. The beam-facing side of the entrance φ2 mm aperture had burn marks with some horizontal elongation from electron and ion impact. Results from Cl⁻ and F⁻ transmission tests are given in Table 8.1 and the ISA settings and schematic are given in Table 8.2. Without the restricting φ2 mm apertures, greater transmission that was less dependent on narrow rf V_{pp} settings was achieved with lower lens voltages.

Subsequently, a pair of φ3 mm apertures were installed at L2 and L3 to test transmission, leaving L4 out and L5 at φ8 mm. Results from Cl⁻ transmission tests are given in Table 8.3 and
the ISA settings and schematic are given in Table 8.4. Despite the presence of φ3 mm entrance apertures, transmission was still very good although there was stronger dependence on the rf $V_{pp}$ settings. These measurements show that it is possible, with relatively large voltages applied to L2 and RFQ4, to focus un-cooled ion beams relevant to ISA studies through the φ3 mm apertures.

8.1.4 Transmission vs. RF1 and RF2 $V_{pp}$ through Tuned ISA

Although Figure 8-2 shows a gradual transmission increase as $q_2$ is raised to 0.3, with some sharp tuning peaks that arise from ‘$q_2$ focussing’, transmission was only 1%. Most of the DC voltages were set to 0 V and φ2 mm apertures were shown to be too small for good vacuum transmission with many of the un-cooled ion beams of interest for current ISA applications.

Application of the lens and RFQ DC voltages increases the complexity of tuning many folds. There are a large number of voltage and rf combinations that lead to peaks in transmission, and the optimum peak settings can be difficult to determine. Moreover, with the DC voltages on, the transmission curves tend to be peaked much more sharply at very specific rf $V_{pp}$ values when both entrance and exit apertures are in place. Based on the information gained from the studies briefly described in section 8.1.3, φ3 mm entrance and exit apertures at L2, L3, L4 and L5 were installed with the second collision cell that incorporated gradient bars.

Figure 8-3 shows the results of rf $V_{pp}$ scans measured at FC3 and FC4. An (NaCl + S) + Nb target (1:3 vol.) was used to generate 1.05 nA $^{37}$Cl– measured at FC2. The ion source was maintained at $V_s = -19.9828$ kV and $\Delta V_{ISAS}$ was set to 5.1 ± 0.1 eV. Pressure and slit values are given in the figure. After tuning the ISA for transmission from FC2 to FC3, the optimum rf $V_{pp}$ setting for one RFQ pair was held fixed and the other scanned. Then the process was repeated to scan the other RFQ pair. Then the process was repeated for transmission measurements at FC4. Unfortunately the system capacitances and rf frequency were not properly optimized, limiting the $V_{pp}$ that could be applied to each RFQ pair and, in turn, limiting the $q_2$ scan range.

The maximum FC2 to FC3 transmission achieved was 81%, worse than that achieved under comparable conditions without the presence of the exit apertures (see Table 8.3), and requiring relatively large DC voltages.

Onset of high transmission was at $q_2 = 0.9$ while scanning RF1 (controlling RFQ1 and RFQ2) and was flat-topped until $q_2 = 0.3$, after which transmission began to decrease. The transmission profile over $0 \leq q_2 \leq 0.3$ is very close to that of an ideal rf quadrupole instrument, with the late onset affected by the initial focussing and suggesting the ion radial energy, $K_r$, is
large (under these conditions \( V^* (r = 1.5 \text{ mm}, q_2 = 0.9) = 10.8 \text{ eV} \), \( V^* \) is the effective potential discussed in section 4.1.2, given by Eq 4.40). The steady decline for \( q_2 > 0.3 \) was not eliminated with tuning.

Conversely, there were three peaks during the RF2 scan (controlling RFQ3 and RFQ4), with lower transmission at each successive peak. Tuning did not compensate for losses. The first pair of quadrupoles need only be tuned to focus onto a pair of closely spaced (~ 0.5 mm) \( \phi 3 \text{ mm} \) apertures. Conversely, RFQ3 must be tuned for a similar \( \phi 3 \text{ mm} \) aperture pair while RFQ4 must simultaneously be tuned for the \( \phi 4 \text{ mm} \) aperture of Co2 downstream. When large transmission is desired with un-cooled ion beams that have large \( K_r \) and large energy spreads, separate \( q_2 \) control before each aperture is desirable when the apertures are small.

The bottom panel shows maximum transmission to FC4. Between FC3 and FC4 is a ‘bouncer magnet’ used for experiments from another branch of the IsoTrace Laboratory AMS system. Although the steerers in AA were used, there is very low transmission through the magnet box and 60% of the ion beam was lost. Both the RF1 and RF2 scans now have a very strong dependence on the chosen \( V_{pp} \) and have very pronounced maxima and minima. As opposed to illustrating a property of rf quadrupole instrument design, the panel is included to show a feature of the current ISA test bed to IsoTrace AMS system coupling.
A 19.9828 keV 1.05 nA (at FC2) beam of $^{37}\text{Cl}^-$ was generated and transmission through the ISA was optimized at $\Delta V_{\text{ISAS}} = 5.1 \pm 0.1$ V. Fixing the voltages at the optimum settings, each rf supply was scanned separately (holding the other fixed). FC2 to FC3 transmission was > 80%. FC3 to FC4 transmission was compromised by a feature of the test bed coupling to the IsoTrace AMS system and is not indicative of the ultimate performance capability of the ISA. It is included to show a feature of the current system.
9 General Transmission in CH$_4$ and Ar

As discussed throughout this thesis, high transmission of the analyte anion with transmission fluctuations that can be reckoned is very important for AMS applications. Some of the most consequential factors affecting transmission through the ISA when gas is used include:

- ISA tuning, including $q_2$ selection (and use of appropriate apertures)
- rf heating (Eq 4.42, depends on $q_2$, see calculation in section 6.3.1 regarding anion losses)
- $\Delta V_{\text{ISAS}}$ (Eq 7.1, difference between initial acceleration voltage and ISA deck deceleration voltage)
- relative anion–gas mass: affects scattering angles and energy loss (eg. Eq 6.21, 6.26), $K_R$ (Eq 6.19, kinetic energy available for conversion in the centre of mass) and $T_e$ (Eq 6.35)
- atomic structure of the ion and neutral (eg. see discussion at Eq 6.27 and section 6.4)
- pressure outside the collision cell in the higher energy regions of the system
- reaction channels, barriers and cross sections
- anion beam energy spread and radial energy $K_r$, and proportions of excited anion states
- excited states of the gas
- gas impurities

With stable and predictable transmission, reactions in the ISA can be used to attenuate isobar signals for trace isotope abundance ratio measurements (see chapter 2 for a discussion of the challenges, typical trace to abundant isotope ratios are $< 10^{-12}$ for AMS). Reactions can be used to convert isobar anion interferences in some way such as electron or atom transfers with the collision gas. It is possible that such mechanisms could be used with the analyte anion for separation from isobars as well. As pointed out by Douglas (1989, discussed in chapter 3) and indicated by some preliminary experiments with the ISA, molecular dissociation via CID has so far proven to be inefficient for isobar separation at the levels currently needed in AMS.

It is also apparent (eg. chapter 5) that ‘cooled’ ions should have higher transmission through smaller apertures than if $K_r$ is large. Cooling also lowers $K_R$ and $T_e$, and collision cross sections may be larger at lower kinetic energy as potential dipole interactions become more significant (see section 6.2 and Sakimoto and Takayanagi 1980, examples in Lindinger et al. 1975). In some cases this will avoid electron detachment and the opening of unwanted reaction
channels. In other cases, however, it may promote unwanted interactions such as possible formation of unwanted weakly-bound adduct compounds or other compounds that may hinder isobar separation or analyte detection (see sections 6.2 and 6.4). Ultimately, experiment determines which gases are best for each isobar system.

### 9.1 Molecular and Atomic Properties

Table 9.1: Molecular Structure, Bond Lengths and Bond Dissociation Energies for N$_2$O, NO$_2$, CH$_4$, O$_3$, O$_2$ and N$_2$

<table>
<thead>
<tr>
<th>Molecular Structure</th>
<th>Bond Lengths</th>
<th>Bond Dissociation Energies</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitrous oxide N$<em>2$O ($C</em>{nv}$)</td>
<td>1.1284 Å ($r_e$)</td>
<td>D 4.934 ± 0.004 eV</td>
</tr>
<tr>
<td>methane CH$_4$ ($T_d$)</td>
<td>1.0870 Å ($r_e$)</td>
<td>D(H-CH$_3$) 4.545 ± 0.004 eV</td>
</tr>
<tr>
<td>nitrogen dioxide NO$<em>2$ ($C</em>{2v}$)</td>
<td>1.93 Å</td>
<td>D(O-NO) 3.1682 ± 0.0013 eV</td>
</tr>
<tr>
<td>oxygen O$_2$</td>
<td>1.2074 Å</td>
<td>D 5.1562 ± 0.0018 eV</td>
</tr>
<tr>
<td>nitrogen N$_2$</td>
<td>1.0977 Å</td>
<td>D 9.7757 ± 0.0010 eV</td>
</tr>
</tbody>
</table>

As compiled in Haynes and Lide (2011). Given in brackets beside the name and molecular formula is the point group of the molecule. Bond distances are given in angstroms (Å = 10$^{-10}$ m) and $r_e$ is for values that represent the hypothetical non-vibrating state ‘equilibrium distance’ (see ibid p. 9-19). These distances are only guides for ‘room temperature’ gases (290 – 300 K). Bond dissociation energies, D, were converted from KJ/mol to eV (see Appendix A). D(N-O$_2$) given for NO$_2$ was calculated from D(O-NO), D(N-O) and D(O-O). Two bond structure variations are given below N$_2$O indicating where the + and – charges would reside (Herzberg 1991 p.369).
Table 9.2: Electron Binding and Dipole Properties for N₂O, NO₂, CH₄, O₃, O₂ and N₂

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>–</td>
<td>15.508</td>
<td>–</td>
<td>2.593</td>
</tr>
<tr>
<td>N₂</td>
<td>–</td>
<td>15.5808</td>
<td>–</td>
<td>1.7403</td>
</tr>
<tr>
<td>N₂O</td>
<td>–0.03 (0.10)</td>
<td>12.886</td>
<td>0.16083</td>
<td>3.03</td>
</tr>
<tr>
<td>NO₂</td>
<td>2.273 (0.005)</td>
<td>9.586 (0.002)</td>
<td>0.316 (0.010)</td>
<td>3.02</td>
</tr>
<tr>
<td>O₃</td>
<td>2.1028 (0.0025)</td>
<td>12.43</td>
<td>0.53373</td>
<td>3.21</td>
</tr>
<tr>
<td>O₂</td>
<td>0.450 (0.002)</td>
<td>12.0697 (0.0002)</td>
<td>–</td>
<td>1.5812</td>
</tr>
</tbody>
</table>

As compiled in Haynes and Lide (2011). Uncertainties (+) are listed when given in the reference. Polarizability is listed as the static average electric dipole polarizability for ground state molecules and is given in cgs units (α [cm³, cgs] = (4πε₀)⁻¹ x 10⁶ α [Cm²/V, SI]).

Table 9.3: Atomic Radius, Electron Binding and Polarizability for Ar, C, Cl, H, N, O and S

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>1.88</td>
<td>–</td>
<td>15.759610</td>
<td>1.6411</td>
</tr>
<tr>
<td>C</td>
<td>1.70</td>
<td>1.262119 (0.000025)</td>
<td>11.26030</td>
<td>1.76</td>
</tr>
<tr>
<td>Cl</td>
<td>1.75</td>
<td>3.612724 (0.000027)</td>
<td>12.96763</td>
<td>2.18</td>
</tr>
<tr>
<td>H</td>
<td>1.09</td>
<td>0.754195 (0.000019)</td>
<td>13.598443</td>
<td>0.666793</td>
</tr>
<tr>
<td>He</td>
<td>1.40</td>
<td>–</td>
<td>24.587387</td>
<td>0.2050522</td>
</tr>
<tr>
<td>N</td>
<td>1.55</td>
<td>–</td>
<td>14.5341</td>
<td>1.10</td>
</tr>
<tr>
<td>O</td>
<td>1.52</td>
<td>1.4611096 (0.0000007)</td>
<td>13.61805</td>
<td>0.802</td>
</tr>
<tr>
<td>S</td>
<td>1.80</td>
<td>2.077103 (0.000001)</td>
<td>10.36001</td>
<td>2.90</td>
</tr>
</tbody>
</table>

As compiled in Haynes and Lide (2011). Uncertainties (+) are given where given in source. Atomic radii are given as the Van der Waals radius. Polarizability is listed as the static average electric dipole polarizability for ground state molecules and is given in cgs units (α [cm³, cgs] = (4πε₀)⁻¹ x 10⁶ α [Cm²/V, SI]), the uncertainty is 2% except for Ar which is 0.05%.
9.2 Cooling in CH\textsubscript{4} and Ar

Methane in its ground state is tetrahedral with a central C atom ‘caged’ by 4 H atoms, and a hard-sphere radius $r \sim 2.1$ Å can be approximated using 2 times the H–CH\textsubscript{3} bond length (Table 9.1). The Van der Waals radius for Ar is $r = 1.88$ Å (Table 9.3). These radii can be used to calculate a hard-sphere cross section, $\sigma_{\text{HS}}$ (Eq 6.28). Although they do not take long-range coulomb forces into account (screened Coulomb scattering or Langevin cross sections), calculations with the hard sphere approximation are useful in getting some idea of the energy losses and number of collisions between an atomic anion and Ar or CH\textsubscript{4} at $> 1$ eV kinetic energy.

As the kinetic energy drops below 1 eV, the polarizabilities ($\alpha$) of Ar and CH\textsubscript{4} can be used to calculate Langevin cross sections, $\sigma_{\text{LGS}}$ (Eq 6.30), since there are no permanent dipole moments (see sections 6.2 and 9.1). These will be larger than $\sigma_{\text{HS}}$ at low enough energy, and since CH\textsubscript{4} is about 40\% the mass of Ar and the polarizability is 1.6 times that of Ar, $\sigma_{\text{LGS}}$ for CH\textsubscript{4} will again be larger than that of Ar for the same lab frame ion kinetic energy.

On the other hand, a single collision can result in greater kinetic energy loss (at larger scattering angle) in Ar than in CH\textsubscript{4} when $K_0$ is much greater than any resultant vibrational or rotational modes of CH\textsubscript{4} since Ar is much more massive. The four fundamental vibrational frequencies for CH\textsubscript{4} listed in Haynes and Lide (2011 p. 9–102) would be equivalent to $< 0.4$ eV each.

As the kinetic energy of an ion approaches the kinetic energy of the gas constituents, the motion of the gas molecules or atoms themselves becomes important and limits the amount of cooling that can be achieved through purely elastic collisions (Baranov 2003, 2004, Baranov et al. 2005). Non-elastic collisions, taking advantage of $Q_{\text{col}}$ in Eq 6.26, could provide a means for cooling ions below the gas ‘temperature’ on average if pressure, cell length and initial ion energy were appropriate. On the other hand, it is also possible for gas molecules in excited states to increase ion kinetic energy through $Q_{\text{col}}$ (details can be found in Cooks 1978).

A rigorous study of cooling would be a fairly complicated undertaking and is left for future work. In order to get an idea of the final ion energies in the ISA collision cell at various pressures, three questions were addressed for this thesis using a hard sphere approximation: 1) the energy loss/final ion energy during a single collision with Ar and CH\textsubscript{4}; 2) the expected number of collisions versus collision cell gas pressure; and 3) the average final energy versus number of collisions, and average number of collisions needed for ion thermalization.
Figure 9-1: Hard Sphere Elastic Collision Kinetic Energy Loss vs. Lab Frame Scattering Angle for Cl on Ar and CH₄

Shown is the final kinetic energy, $K_f$, normalized to initial lab frame kinetic energy, $K_0$, for hard sphere elastic scattering of $^{35}$Cl from targets $^{40}$Ar and $^{12}$CH₄ assuming stationary targets. Solid lines show energy versus lab frame scattering angle (Eq 6.12), dash-dot lines show energy versus CM frame scattering angle (Eq 6.22). Conversion between the scattering angles of the two coordinate systems can be accomplished using Eq 6.18. The CM frame angle distribution has a larger proportion of lab frame low-scattering angles.

The maximum lab frame scattering angle for Cl from CH₄ is $27.2^\circ$ ($\theta_{max}$, Eq 6.12). The minimum $K_f/K_0$ represents a head-on collision ($\theta = 0^\circ$) while the maximum is for no scattering ($\theta = 0^\circ$). Any angle is possible for Cl scattering from Ar and in a head-on collision ($\theta = 180^\circ$) $K_f$ is not 0 and Cl recoils in a direction opposite to the direction of initial approach. The average $K_f$ shown in the legend was calculated using the lab frame curves assuming all possible scattering angles to be equally likely. Values $m_2/m_1$ are given for cross reference with Figure 6-3.
Figure 9-1 shows the final kinetic energy, $K_f$, normalized to the initial lab frame kinetic energy, $K_0$, of a Cl atom with Ar and CH$_4$ (assumed at rest) in ‘free drift’, meaning that external accelerating fields were not considered. In CH$_4$, since Cl is more massive, the maximum scattering angle in the lab frame is $\theta_{\text{max}} = 27.2^0$ (Eq 6.12), while Cl can scatter at any angle in Ar. In particular, smaller losses from scattering may be expected in CH$_4$ than in Ar with Cl. On the other hand, there is greater average kinetic energy transfer in Ar than in CH$_4$. On average, a Cl atom will lose over 2/3 of its initial kinetic energy in Ar versus 50% in CH$_4$, assuming all lab frame scattering angles equally likely. However, referring to Figure 6-3, the energy available for conversion, $K_R$ (Eq 6.19), is 0.53$K_0$ in Ar versus only 0.31$K_0$ in CH$_4$, so that there is less energy available for electron detachment from Cl$^-$ in CH$_4$. This is particularly relevant during initial collisions with larger $K_0$.

Figure 9-2 shows the probability for $x$ collisions, $P_C(x)$ (Eq 6.34), between Cl and Ar ($T = 300K$) at several ISA collision cell pressures, $P$, using a hard sphere cross section, $\sigma_{\text{HS}}$ (Eq 6.28, with the Van der Waals radii of Cl and Ar in Table 9.3) and cell length $l = 150$ mm. This represents a lower limit as the ion path length is greater than $l$ because of oscillations in the rf field and because the collision cross section increases as ion kinetic energy approaches 0.025 eV ($\sigma_{\text{LGS}}$, Eq 6.30, Ar has no permanent dipole moment).

Similar values would be expected for atomic anions of similar size to Cl, and for CH$_4$ which should have larger cross sections than Ar. The expectation values represent the average number of collisions expected at the indicated pressures. In general, at 6 mTorr cell pressure Ar or CH$_4$, more than 12 collisions with Cl or S would be expected.

Next, MATLAB 7.0 was used to perform a calculation on 2000 projectiles using the hard sphere ‘free drift’ elastic scattering model. Projectiles of mass $m_1 = 35$ amu (Cl), 147 amu (SrF$_3$) and 300 amu, with $K_0 = 15$ or 5 eV, collided with targets of mass $m_2 = 4, 16$ or 40 amu (He, CH$_4$ or Ar), assumed at rest. A random lab frame projectile scattering angle ($\leq \theta_{\text{max}}$ when $m_2 < m_1$) was assigned to each collision, assuming all angles equally probable, and Eq 6.12 was used to calculate $K_f$. The process was repeated until $K_f \leq 0.025$ eV at which point $K_f$ was set to 0.025 eV and the number of collisions, $x$, required to reach this energy was recorded. Figure 9-3 and Figure 9-4 show the results.

The top panels show the average energy of the 2000 projectiles versus the number of collisions. The bottom panels give the proportion of the population that reached 0.025 eV at $x$
collisions (not the average population that had been thermalized, but the average proportion that required x collisions to be thermalized). Mass 300 amu on Ar, SrF$_3$ on CH$_4$ and Cl on He all had similar cooling statistics under this scenario, requiring 30 – 40 collisions for thermalization of all 2000 projectiles with $K_0 = 15$ eV and 30 – 35 collisions for $K_0 = 5$ eV. For both $K_0$, the Cl projectiles were cooled by $x = 12.5$ collisions in both CH$_4$ and Ar.

Figure 9-2: Expected Number of Collisions vs. ISA Collision Cell Pressure for Cl on Ar

The probability for x collisions at pressure P, $P_c(x)$ (Eq 6.34), was calculated using a hard sphere cross section, $\sigma_{HS}$ (Eq 6.28, with Van der Waals radii of Cl and Ar in Table 9.3), for Cl on Ar gas at $T = 300K$ in a collision cell of length $l = 150$ mm. This provides a lower limit as the actual path length of the ions will be greater than $l$ because of oscillations in the rf field and because the collision cross section will increase as the ion kinetic energy approaches thermal according to $\sigma_{LGS}$ (Eq 6.30, Ar has no permanent dipole moment). The expectation value of the number of collisions at pressure P, $<x(P)> = \sum_{x=1}^{50} x \cdot P_c(x, P)$, was also calculated using $x = 50$ as an upper limit as $P_c(50, P) < 10^{-9}$ for all P considered.
Using a hard sphere elastic scattering ‘free drift’ (external accelerating fields not considered) model, the final kinetic energy, \( K_f \), of 2000 ions with initial lab frame kinetic energy, \( K_0 = 15 \text{ eV} \), was calculated using Eq 6.12 with random scattering angles at each collision assuming the gas atoms / molecules were at rest. When \( K_f \leq 0.025 \text{ eV} \), the calculation set \( K_f = 0.025 \text{ eV} \) and recorded the number of collisions required to reach this value for each ion. The top panel shows the average \( K_f \) of the 2000 ions versus the number of collisions. The bottom panel shows the average proportion of the 2000 atoms thermalized at \( x \) collisions. This represents the average number of collisions required for thermalization. For example, on average 15% of SrF\(_3\) ions would be expected to be cooled on the 10\(^{th}\) collision with Ar in this model. Mass ratios \( m_2/m_1 \) are provided for cross reference with Figure 6-3.
Figure 9-4: Average Kinetic Energy vs. Number of Collisions and Average Number of Collisions Required for Thermalization for $K_0 = 5 \text{ eV}$

Using a hard sphere elastic scattering ‘free drift’ (external accelerating fields not considered) model, the final kinetic energy, $K_f$, of 2000 ions with initial lab frame kinetic energy, $K_0 = 5 \text{ eV}$, was calculated using Eq 6.12 with random scattering angles at each collision assuming the gas atoms / molecules were at rest. More details can be found in the caption for Figure 9-3.

9.2.1 Discussion

There is a greater rate of cooling per collision on average in Ar than in CH$_4$. On the other hand, for anions between the masses of Ar and CH$_4$ (eg. Cl$^-$ and S$^-$), the range of possible scattering angles is significantly greater in Ar, with back-scattering possible, likely resulting in greater ion losses during initial collisions at larger $K_0$. For lower masses, the amount of kinetic energy retained for back-scattering is greater. Not only does this require stronger gradients to maintain forward motion and focus ions through apertures, but this can cause scatter induced anion heating. An anion scattering at an appropriate rf phase can actually enter a region of deeper
rf potential and experience an overall gain in kinetic energy as the rf voltage increases.

Furthermore, $K_R$ is significantly greater in Ar than in CH$_4$ (by a factor of 1.7 in the case of Cl$^-$, see Figure 6-3) resulting in more energy available for electron detachment. More collisions are also expected with CH$_4$ than with Ar on average for equivalent cell pressures because of the larger hard sphere and Langevin cross sections. On the other hand, screened Coulomb scattering effectively increases the relative proportion of smaller angle scattering events. The hard sphere model likely over-estimates the absolute rate of cooling in a particular gas, but is still a useful estimate for the relative rate of cooling in different gases.

Within the limitations of the approximations used, the number of collisions needed for Cl thermalization in Ar and CH$_4$ were not drastically different, amounting to less than 6 mTorr cell pressure in the ISA for $K_0 = 5$ eV ions (a typical value). Consideration was neither given to rf heating nor to motion of the gas particles. The kinetic energy loss calculations also did not account for excitation of vibrational and rotational states of CH$_4$ that could increase the rate of energy loss per collision, particularly significant below 0.5 eV. With these considerations, CH$_4$ is a much more attractive cooling gas for the less massive anions than Ar.

For more massive anions, more massive cooling gases could be used. For example, the maximum elastic lab frame hard sphere scattering angle for SrF$_3$ on Ar would be 15.8$^\circ$ and $K_R = 0.21K_0$. From Figure 9-3 and Figure 9-4, the same amount of cooling in Ar would be achieved with less than half of the collisions required for CH$_4$ at $K_0 = 15$ and 5 eV. Under such conditions Ar may be much more attractive.

### 9.3 ISA Transmission for Various Anions in CH$_4$ and Ar, and Cl$^-$ and CN$^-$ in NO$_2$

Analogous to Figure 6-2 in section 6.3.1, Figure 9-5 shows the transmissions for various anions with 6 mTorr CH$_4$, Ar or NO$_2$ in the collision cell versus $T_e$ (Eq 6.35 using electron affinities, EA, for $\Delta b$). Data was taken over 3 years with various $\Delta V_{ISAS}$ using the cell with gradient bars and aperture diameters $\phi L_2$, L3, L4, L5 = 3 mm (Figure 7-4). In the cases of Cl$^-$ and CN$^-$ + NO$_2$, $\Delta b = EA$(Cl or CN) rather than accounting for EA(NO2) or oxygen affinities. Although electron and O transfer is possible, and NO$_2$ has proven to be highly reactive with many anions, no significant levels of anion reaction products were observed with these systems.
These data represent what are most likely highly un-reactive collisions. Data and calculations are listed in Table 9.4.

For all measurements, $V_s = -20$ kV (sputter source acceleration voltage) with a variation of $0.5$ kV over the range of data, and typical AMS settings were used (section 7.6). With the exception of CN$^-\,$ that was measured at FC5 (not suppressed) using $q = +2$ after the tandem accelerator and $45^\circ$ electric analyzer, all measurements were done with FC7 using the full AMS system (Figure 7-1), stripping to $q = +3$.

In the ISA (see Figure 7-4), measurements reported here were made with $q_2 < 0.3$ for all quadrupole sections (RFQ1 – RFQ4) and the static offset voltage on the quadrupole rods inside the cell was set to RFQ3 DC = 0 V. An example of typical settings for other components can be found in Table 10.1 (settings for Figure 10-1) and Table 10.2.

So far, all anion-gas attenuations observed with the ISA have tended to have a plateau that begins near or has fully onset by $P = 6$ mTorr cell pressure. Tuning at $P > 5$ mTorr has tended to yield the most consistent transmission results, likely because the majority of anions in the anion beams under study had been cooled (as discussed in the last section). Furthermore, there exists more transmission data for $P = 5 – 7$ mTorr than at other pressures.

Base pressure (no gas leaking into the collision cell) transmission from FC2 to the final detector can be used as an index for the comparability of tuning conditions. The base pressures ($P_{isa} = 1$ to $2 \times 10^{-7}$ Torr, $P_{FC3} = 0.8 – 2 \times 20^{-7}$ Torr) and base pressure transmissions of these data were also relatively consistent. Transmission FC2 to FC7 (FC5 for CN$^-\,$) at 6 mTorr cell pressure in Figure 9-5 is normalized to the base pressure transmission during the given measurement (more information in Table 9.4).

Measurement uncertainties with the ISA were dominated by tuning uncertainties. For example, transmission could be affected drastically by small changes to $q_2$ (see Figure 8-3). Although tuning was done carefully, differences in absolute transmissions on a given day were as much as 20% at the various stages of development, and sometimes larger for measurements made earlier in the project.

### 9.3.1 Observed Trends in Anion Losses with CH$_4$, Ar and NO$_2$

According to the fairly simplistic approximations in section 9.2, most of the anions emanating from the collision cell at 6 mTorr Ar and CH$_4$ would have had near thermal kinetic energy. If scattering losses were very much different for the anion-gas systems studied then the...
Table 9.4: Transmission Data for Various Anions in Ar, NO₂ and CH₄

<table>
<thead>
<tr>
<th>Gas</th>
<th>Anion (X⁻)</th>
<th>ΔV_{ISAS} [V]</th>
<th>Kᵣ [eV]</th>
<th>Tₑ [eV]</th>
<th>FC₂ [nA]</th>
<th>Pisa [x 10⁻⁷ Torr]</th>
<th>Transmission (%) Base Pressure</th>
<th>6 mTorr (±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>³⁷Cl⁻</td>
<td>5.1</td>
<td>2.65</td>
<td>-0.96</td>
<td>5.0</td>
<td>1.0</td>
<td>8</td>
<td>29 (6)</td>
</tr>
<tr>
<td></td>
<td>³⁵Cl⁻</td>
<td>6.0</td>
<td>3.20</td>
<td>-0.413</td>
<td>380</td>
<td>1.1</td>
<td>5.2</td>
<td>25 (5)</td>
</tr>
<tr>
<td></td>
<td>³²S⁻</td>
<td>4.8</td>
<td>2.67</td>
<td>0.59</td>
<td>5.2</td>
<td>2.1</td>
<td>14.1</td>
<td>18 (5)</td>
</tr>
<tr>
<td></td>
<td>³²S⁻</td>
<td>6.6</td>
<td>3.67</td>
<td>1.59</td>
<td>7</td>
<td>1.6</td>
<td>11.2</td>
<td>19 (5)</td>
</tr>
<tr>
<td></td>
<td>¹²C¹⁴N⁻</td>
<td>9.8</td>
<td>5.94</td>
<td>2.08</td>
<td>0.090</td>
<td>2.1</td>
<td>20.6²</td>
<td>11.4⁴ (4)</td>
</tr>
<tr>
<td></td>
<td>¹²C₃⁻</td>
<td>8.0</td>
<td>4.21</td>
<td>2.23</td>
<td>13</td>
<td>2.0</td>
<td>9.2⁹</td>
<td>8⁶ (2)</td>
</tr>
<tr>
<td></td>
<td>²⁷Al⁺</td>
<td>6.6</td>
<td>3.94</td>
<td>3.50</td>
<td>13.5</td>
<td>1.1</td>
<td>9.1</td>
<td>0.76 (0.2)</td>
</tr>
<tr>
<td></td>
<td>³²S¹⁶O⁻</td>
<td>4.8</td>
<td>2.18</td>
<td>1.06</td>
<td>0.780</td>
<td>1.1</td>
<td>7.5⁹</td>
<td>25⁶ (5)</td>
</tr>
<tr>
<td></td>
<td>³²S¹⁶O⁻</td>
<td>6.2</td>
<td>2.82</td>
<td>1.69</td>
<td>0.120</td>
<td>2.6</td>
<td>12.5⁹</td>
<td>22⁶ (5)</td>
</tr>
<tr>
<td>NO₂</td>
<td>³⁷Cl⁻</td>
<td>5.1</td>
<td>2.83</td>
<td>-0.79</td>
<td>3.3</td>
<td>2.1</td>
<td>6.6</td>
<td>39 (10)</td>
</tr>
<tr>
<td></td>
<td>³⁵Cl⁻</td>
<td>5.0</td>
<td>2.84</td>
<td>-0.77</td>
<td>11.5</td>
<td>0.95</td>
<td>10.4</td>
<td>36 (10)</td>
</tr>
<tr>
<td></td>
<td>¹²C¹⁴N⁻</td>
<td>9.8</td>
<td>6.26</td>
<td>2.40</td>
<td>0.090</td>
<td>2.1</td>
<td>20.6²</td>
<td>20² (6)</td>
</tr>
<tr>
<td>CH₄</td>
<td>³⁷Cl⁻</td>
<td>4.7</td>
<td>1.42</td>
<td>-2.19</td>
<td>3.2</td>
<td>1.2</td>
<td>9.4</td>
<td>90 (20)</td>
</tr>
<tr>
<td></td>
<td>³⁷Cl⁻</td>
<td>4.7</td>
<td>1.42</td>
<td>-2.19</td>
<td>0.900</td>
<td>1.2</td>
<td>10</td>
<td>85 (17)</td>
</tr>
<tr>
<td></td>
<td>³⁷Cl⁻</td>
<td>5.1</td>
<td>1.54</td>
<td>-2.07</td>
<td>3.2</td>
<td>2.1</td>
<td>6.9</td>
<td>77 (15)</td>
</tr>
<tr>
<td></td>
<td>³²S⁻</td>
<td>4.7</td>
<td>1.57</td>
<td>-0.51</td>
<td>3.6</td>
<td>1.2</td>
<td>6.5</td>
<td>60 (12)</td>
</tr>
<tr>
<td></td>
<td>¹²C¹⁴N⁻</td>
<td>9.8</td>
<td>3.73</td>
<td>-0.129</td>
<td>0.090</td>
<td>2.1</td>
<td>20.6²</td>
<td>46² (15)</td>
</tr>
<tr>
<td></td>
<td>³²S⁻</td>
<td>4.7</td>
<td>1.57</td>
<td>-0.51</td>
<td>1.6</td>
<td>1.2</td>
<td>2.8</td>
<td>39 (20)</td>
</tr>
<tr>
<td></td>
<td>²⁹Si⁻</td>
<td>6.6</td>
<td>2.35</td>
<td>0.96</td>
<td>1.5</td>
<td>1.0</td>
<td>14.2</td>
<td>19 (4)</td>
</tr>
<tr>
<td></td>
<td>¹²C⁻</td>
<td>5.1</td>
<td>2.91</td>
<td>1.65</td>
<td>0.270</td>
<td>1.0</td>
<td>10.7</td>
<td>2.27 (0.05)</td>
</tr>
</tbody>
</table>

See next page for caption.
strong linearity of the curves for transmission vs. $T_e$ (Eq 6.35), with $T_e = K_R - E_A(X)$ ($K_R$ from Eq 6.19, $E_A$ the electron affinity of an element, $X$) would not be expected.

To that end, $SO^-$ appears to have had better transmission in Ar than the other anions studied, and represents the only anion that had larger mass than Ar so that it is not unreasonable to expect less scattering losses. On the other hand, with the limited data available, the pattern of $SO^-$ loss with $T_e$ appears to be consistent with the less massive anions. The larger transmission could represent less base pressure loss due to scattering, while the increase in transmission with decrease in $T_e$ would still represent electron detachment losses. Because $SO^-$ was the only anion with larger mass than Ar, the data was excluded from the linear fit. Likewise, $C^-$ was the only anion less massive than $CH_4$ and this point was excluded from the $CH_4$ linear fit.

Nonetheless, the linearity of the curves in Figure 9-5 gives a strong indication that all of the anions studied behaved similarly in Ar and $CH_4$ at 6 mTorr. Linearity is not with $K_R$, mass or $E_A$ alone, but from calculation of $T_e = K_R - E_A(X)$, suggesting that a major source of loss was electron detachment. Although limited, the data continue to rise into the $-T_e$ range. Sputtering is a relatively violent anion production method and atomic anion beams can be expected to have especially large energy distributions and molecular anions may have sizable populations in excited vibrational, electronic and rotational states. Unfortunately, electron detachment threshold energies cannot be predicted at present with these data because information is known for only two points that do not span a large portion of the data range ($Cl^- + Ar$ electron detachment threshold energy is $7.3 \pm 0.2$ eV, Smith et al. 1978).
For the heavier gases, NO$_2$ and Ar, except for SO$^-$ + Ar, anion scattering could have proceeded at any angle. This can lead to larger than expected anion losses and even scatter induced anion heating. For example, if a collision happened at a low field phase of the rf cycle, an anion could be back scattered into a deeper region of the potential well and, rather than be cooled, actually experience an overall increase in kinetic energy and trajectory amplitude.

On the other hand, transmission through NO$_2$ is generally found to be higher than through Ar when reactions are not a significant loss mechanism, even though the NO$_2$ molecule is more massive by 6 amu. Referring to Table 9.1 and Table 9.3, the N-O bond length is larger than the Van der Waals radii of N and O. Depending on the molecular orientation, the anion may experience a ‘softer’ collision, interacting more with components of the molecule, and vibrational and rotational excitation of the molecule may also decrease the rate of energy loss in a head-on collision. Moreover, this may also reduce the average scattering angle at higher energies. Conversely, Ar may act more like a hard sphere.
Table 9.4 provides data with normalization and $T_e$ calculations. Briefly, $K_R$ (Eq 6.20) was calculated using $q\Delta V_{ISAS}$ (Eq 7.1, $q = |ne| = 1$ for anion charge), the masses of the anions (neutral mass used) and gas atomic or molecular masses. When $T_e < 0$ (Eq 6.35), electron detachment is not energetically favourable based on EA (electron affinity) and $K_R$ with deceleration to $q\Delta V_{ISAS}$. This neither accounts for the electron detachment threshold energy, which may be more than EA (see text and section 6.3.1), nor for the energy spread of the ion beam. However, the linearity of the data suggests that these anions behaved similarly at 6 mTorr collision cell pressure in the ISA with Ar and CH$_4$. Searches for anion products from these anion – gas systems did not reveal significant levels of anion products. Combined with the linearity of the curves, this suggests that electron detachment and scattering are very significant sources of anion loss with the present system. The SO$^-$ data were not included in the Ar linear fit calculations because these were the only two anions with mass larger than Ar. Likewise, the C$^-$ datum was not included in the CH$_4$ linear fit because it was the only anion less massive than the collision gas. Measurements were made with $q_3 < 0.3$ on RFQ1 – RFQ4, and RFQ3 DC = 0 V (see Figure 7-4). Uncertainties shown are for absolute transmission and are systematic, depending mostly on ISA tuning.
10 \( C_3^- \), \( Cl^- \), \( S^- \) and \( SO^- \) Attenuations and Reactions with Gases: RF Quadrupole Accelerator Mass Spectrometry for the Study of Gas-Phase Anion Reactions

Although \(^{36}\text{Ar}\) is closer in mass to \(^{36}\text{Cl}\) (\(\Delta m = 1.39m_e\), \(m_e\) is the mass of an electron, calculations in Appendix D), the major atomic isobaric interference for \(^{36}\text{Cl}^-\) measurements by AMS is \(^{36}\text{S}^-\) (neutral \(\Delta m = 2.23m_e\)). At equal signal intensity, resolution of \(^{36}\text{S}^-\) from \(^{36}\text{Cl}^-\) would require \(m/\Delta m = 3 \times 10^4\), and at \(^{36}\text{Cl}^-/^{36}\text{S}^- = 10^{-6}\) would require \(6 \times 10^4\) resolving power (assuming Gaussian peak shapes, discussed in section 2.3 and Appendix E).

As discussed in Appendix D, atomic isobars are generally closer in mass than an atomic and a molecular isobar. However, the molecular destruction in tandem accelerators can be used to help resolve fragments from atomic and molecular isobars. Currently, AMS by tandem accelerator requires systems with \( \geq 6 \text{ MV} \) accelerators for \(^{36}\text{Cl}\) analysis (see discussion in sections 2.2 – 2.4).

Briefly, the ISA project was motivated (Doupé et al. 2004) by the measurement of a very large thermal reaction rate constant for \(S^- + \text{NO}_2 \rightarrow \text{NO}_2^- + S\), \(k = 1.3 \times 10^{-9} \text{ cm}^3/\text{s}\), by Dunkin et al. (1972) using a flowing afterglow system, versus a very low \(\text{Cl}^-\) attenuation (50%, fig. 3, ibid).

After a preliminary test of the interactions at low kinetic energy (1 – 15 eV lab frame) using an electrospray ion source and rf quadrupole collision cell-mass spectrometer at IONICS Mass Spectrometry Group Inc (formerly in Concord, Ontario, now Bolton, Ontario, Canada), initial planning and design for the ISA commenced (Litherland et al. 2007).

Working as part of the IsoTrace Laboratory group involved in the project, this PhD project commenced with helping design and build the ISA test bed and box AA following the ISA, with some limited input into the deceleration and acceleration stages of the ISA. The ISA was designed by the IONICS group.

Initially the goal of the project was to have a system that could achieve adequate \(S^-\) - \(\text{Cl}^-\) isobar separation to allow \(^{36}\text{Cl}\) measurements within the \(\sim 2 \text{ MV}\) limit of the IsoTrace AMS system. It was believed that an initial cooling cell, possibly using Ar, would be needed before a second reaction cell with \(\text{NO}_2\) gas were used for isobar separation. Only one collision cell was
initially used in order to minimize the complexity of an already complex system. For many reasons, while the original collision cell has been modified and replaced, use of two collision cells in series has not been attempted and may not be necessary for isobar separation applications.

In order to better understand several of the anion-gas attenuation channels observed, and the onset of what appeared to be attenuation plateaus, several anion-gas reaction channels were studied. Particular emphasis was placed on potential cooling and isobar attenuation reaction gases for the $\text{S}^– – \text{Cl}^–$ anion system, and the results are presented in this chapter. However, these and related studies for other anion systems (see chapter 12), led to the development of a new analytical technique.

Presented in this chapter is the first use of rf quadrupole accelerator mass spectrometry for the study of gas-phase anion reactions, RFQ–AMS–GPAR. An outline of the method is given in section 7.7. It has several advantages over traditional methods of gas-phase chemistry studies.

- First, there is an inherent advantage to AMS sputter sources as they quite readily produce a wide variety of anion species at varying efficiencies depending on the sputter target matrix.
- Second, AMS has unsurpassed sensitivity and a very large dynamic range (over 16 orders of magnitude) so that even very weak signals can be detected (on the order of counts per day).
- Third, AMS can be used for particle identification so that atomic components of a molecule can be determined relatively unambiguously.

For most isobar separation applications, especially those involving more massive anions (eg > 60 amu), it may not be necessary to have more than one collision cell. However, as will be discussed, the typically large kinetic energy distributions associated with several keV kinetic energy Cs$^+$ sputtering for atomic and smaller molecular anion beam production must be considered for gas-phase reaction studies (see section 10.3.6). A cooling cell incorporated before the reaction cell is likely necessary for moderation of the anion kinetic energy and to reduce the ion beam energy spread. Collisions would also help de-excite anions in excited states.
10.1 Cl– + Air, Ar, CH4 and NO2

Figure 10-1: Representative $^{35}$Cl– Transmissions through Ar, Air, CH4 and NO2 with $\Delta V_{\text{ISAS}} = 5.1$ V

<table>
<thead>
<tr>
<th>Hard Sphere Lower Limit to Expected Number of Collisions in Ar$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 2 4 6 8 10 12 16</td>
</tr>
<tr>
<td>1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3</td>
</tr>
<tr>
<td>most ions near thermal energy in CH4 and Ar in hard sphere 'free drift' model$^a$</td>
</tr>
</tbody>
</table>

(a) based on the hard sphere approximations in section 9.2 (see Figure 9-2 and Figure 9-4).

Target material was (NaCl + S) + Nb (1:3 vol), ion source $V_s = -19.9828$ V, $\Delta V_{\text{ISAS}} = 5.1$ V and typical settings were used (section 7.6) for $^{35}$Cl$^- \rightarrow ^{35}$Cl$^{+3}$ detection at FC7. Transmission at each pressure was normalized to the base pressure current at FC7 (Pisa = 1 x $10^{-7}$ Torr) for each series of measurements (injecting FC2 = 4.4 – 5.2 nA Cl–), and base pressure FC2 to FC7 transmission was 6.1% (all measurements > 200 pA at FC7). Tuning was done for air transmission only and was not optimized for other gases. See Table 10.1 for ISA settings. The following list provides $K_R$ (Eq 6.20) and $T_e$ (Eq 6.35 with $\Delta_b = \text{EA(Cl)}$) calculations [eV]: Ar 2.72, -0.89; N2 2.27, -1.35; O2 2.44, -1.18; CH4 1.60, -2.01; NO2 2.90, -0.72.

Figure 10-1 shows representative plots of Cl$^-$ transmission through Ar, air, CH4 and NO2 measured at FC7 (full AMS system) with $^{35}$Cl$^- \rightarrow ^{35}$Cl$^{+3}$ using typical settings (section 7.6). The first 3 gases were tested for cooling purposes while good Cl$^-$ transmission through NO2 is...
essential if NO$_2$ is to be used for S$^{-}$ suppression. A schematic of the AMS system can be found in chapter 7, with symbols defined in Figure 7-1.

The test bed ion source deck $V_s = -19.9828$ kV (Keithley meter reading) with a Nb + (NaCl + S) target (3:1 vol) and $\Delta V_{ISAS} = 5.1$ V. Settings for the ISA were chosen by tuning Cl$^{-}$ + air for maximum transmission FC2 – FC7 at 17 collision cell pressures between 0 and 9 mTorr. Settings for 3 pressures can be found in Table 10.1. Base pressure (Pisa = $1 \times 10^{-7}$ Torr, PFC3 = $0.5 \times 10^{-7}$ Torr) FC2 to FC7 transmission was 6.1% with 4.4 to 5.2 nA $^{35}$Cl$^{-}$ at FC2. Values of $K_R$ (Eq 6.20) and $T_e$ (Eq 6.35) are given in the figure caption.

Uncertainty in absolute transmission was again dominated by uncertainty with ISA tuning and represents a systematic uncertainty for these measurements. Otherwise, there are four main branches of transmission loss that should be considered: scattering, electron detachment, ion–molecule reactions, and tuning through apertures. Tuning was done only with air and was not optimized for the other gases as additional tuning would have required a great deal of time.

Table 10.1: Representative ISA Settings for Figure 10-1 and Figure 10-2

<table>
<thead>
<tr>
<th>$q_2$ values are quoted for $^{35}$Cl$^{-}$.</th>
<th>Cy1</th>
<th>Co1</th>
<th>RFQ1 DC</th>
<th>L1</th>
<th>RFQ2 DC</th>
<th>L2</th>
<th>RFQ3 DC</th>
<th>L5</th>
<th>RFQ4 DC</th>
<th>Co2</th>
<th>Cy2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base pressure is given x $10^{-7}$ Torr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Figure 10-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Base Pressure (Pisa = 1)</td>
<td>1660</td>
<td>4190</td>
<td>46</td>
<td>18</td>
<td>10</td>
<td>200</td>
<td>7</td>
<td>50</td>
<td>85</td>
<td>4000</td>
<td>1820</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>410 ($q_2 = 0.192$)</td>
<td>60</td>
<td>15</td>
<td>100</td>
<td>270 ($q_2 = 0.127$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5 mTorr</td>
<td>1660</td>
<td>4190</td>
<td>46</td>
<td>56</td>
<td>10</td>
<td>120</td>
<td>0</td>
<td>60</td>
<td>85</td>
<td>4000</td>
<td>1820</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>420 ($q_2 = 0.197$)</td>
<td>25</td>
<td>11</td>
<td>25</td>
<td>280 ($q_2 = 0.131$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 mTorr</td>
<td>1660</td>
<td>4160</td>
<td>36</td>
<td>56</td>
<td>10</td>
<td>120</td>
<td>0</td>
<td>45</td>
<td>85</td>
<td>4000</td>
<td>1820</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>420 ($q_2 = 0.197$)</td>
<td>2</td>
<td>25</td>
<td>15</td>
<td>280 ($q_2 = 0.131$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Figure 10-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Base Pressure (Pisa = 1.2)</td>
<td>1650</td>
<td>3600</td>
<td>48</td>
<td>4</td>
<td>0</td>
<td>150</td>
<td>0</td>
<td>150</td>
<td>70</td>
<td>4000</td>
<td>1820</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>238 ($q_2 = 0.112$)</td>
<td>20</td>
<td>0</td>
<td>50</td>
<td>795 ($q_2 = 0.373$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 mTorr</td>
<td>1650</td>
<td>3600</td>
<td>55</td>
<td>8</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>150</td>
<td>75</td>
<td>4000</td>
<td>1820</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>208 ($q_2 = 0.098$)</td>
<td>25</td>
<td>15</td>
<td>50</td>
<td>775 ($q_2 = 0.363$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The appearance of plateaus and very low rates of transmission loss at higher cell pressures indicates that reactions were either not a dominant source of ion loss under the experimental conditions or that reaction equilibrium conditions had been reached. This question was addressed for Ar and NO$_2$ (discussed later this chapter) but, unfortunately, it was not possible to conduct a very thorough investigation due to time and funding restraints.

Tuning may have had some influence on the relatively large drop in CH$_4$ transmission between 3 and 6 mTorr. It should be noted, however, that $\Delta H = 15.9$ kJ/mol (0.165 eV) for Cl$^-$ + CH$_4$ $\rightarrow$ CH$_4$Cl$^-$ (Hiraoka et al. 2001) and this endothermic reaction was not studied. Given the expected amount of cooling that can be estimated from the hard sphere calculations of section 9.2 for the experimental conditions, the possibility of a drop in the Cl$^-$ signal from such reactions merits further investigation. Such an anion could be continually formed and destroyed under appropriate ISA conditions. Hiraoka et al. (2001) give $\Delta H = 14.6$ kJ/mol (0.151 eV) for a further reaction, CH$_4$Cl$^- + 2$(CH$_4$) $\rightarrow$ C$_2$H$_8$Cl$,^-$ but this likely has a relatively low yield at lower pressures in a shorter cell.

Likewise, the full extent that tuning had on the transmission decreases in Ar and NO$_2$ after 5 mTorr is not fully certain as scattering will be different for these gases than air, and back-scattering is possible in Ar and NO$_2$ but not for O$_2$ and N$_2$. The slope of the initial transmission drop between base pressure and the onset of the plateau is affected by scattering, electron detachment and reactions. Reactive losses will be discussed in the next section but were found to account for a negligible portion of these losses.

Nonetheless, the semi-quantitative transmissions shown in Figure 10-1 are useful in demonstrating general trends and the order of attenuation that can be expected in a system like the ISA test bed when reaction rates are low with these K$_R$, T$_e$, gases and optics. Unfortunately, as can also be gleaned from Figure 9-5, Cl$^-$ transmission losses above 5 mTorr with a single collision cell using NO$_2$ or Ar with the current system (especially due to apertures and and inadequate differential pumping) can generally be expected to be in the range of 70%. The system was not ion-optically designed for direct electric deceleration to $\Delta V_{\text{ISAS}} < 4$ V. Transmission through NO$_2$ is again higher than through Ar for the given pressure ranges and $\Delta V_{\text{ISAS}}$. A possible explanation has been outlined at the end of section 9.3.1. The expected NO$_2$ gas NO$_2$/N$_2$O$_4$ molecular ratio has been addressed in section 7.5.1, and should be $> 99.994\%$ NO$_2$ at 6 mTorr. Conversely, transmission through CH$_4$ can be much larger under appropriate conditions (Figure 9-5 and Figure 10-1).
10.1.1 Preliminary Investigation of Potential Reactive Losses for Cl− with Ar and NO₂

A scan of the potential reaction products, $^{35}\text{Cl}^{-} + (\text{Ar + impurities}) \rightarrow ^{35}\text{Cl}^{16}\text{O}_{x}^{-} \rightarrow \text{(AMS)}^{35}\text{Cl}^{+3} (x = 1, 2)$ using FC7 was conducted with typical settings (section 7.6) to see if losses in Ar could be accounted for by oxide gas impurities. ISA settings were the same as those for Figure 10-2 in Table 10.1. For ClO$^{-}$, $q_{2} < 0.249$ and for ClO$_{2}^{-}$, $q_{2} < 0.190$ in the collision cell and following quadrupole segment, well within a good transmission range. Furthermore, the resultant molecular anion, when more massive than the initial anion, is effectively cooled because of the increase in mass. Injecting ClO$_{2}^{-}$ using the Cl$^{-}$ ISA settings indicated that the uncooled ClO$_{2}^{-}$ transmission was within 10% of transmission with optimum ClO$_{2}^{-}$ tuning.

No significant (ClO$_{x}^{-}$/Cl$^{-} < 10^{-6}$) levels of $^{35}\text{Cl}^{16}\text{O}^{-}$ or $^{35}\text{Cl}^{16}\text{O}_{2}^{-}$ up to 8 mTorr Ar were found while injecting 230 nA $^{35}\text{Cl}^{-}$ with $\Delta V_{\text{ISAS}} = 6.0$ V ($V_{s} = -20.7$ kV, Nb + (NaCl + S), 3:1 vol. target). This represents larger average $K_{R}$ than for the curve in Figure 10-1. Transmission at base pressure ($P_{\text{isca}} = 1.1 \times 10^{-7}$ mTorr) FC2 to FC7 was 5.2%. At 8 mTorr Ar in the cell, the Cl$^{-}$ transmission relative to base pressure was 26%, consistent with Figure 10-1 and Figure 9-5. Stripping yield would only account for a difference of 35% between the Cl$^{+3}$ signals from Cl$^{-}$ and ClO$^{-}$ at FC7 (section 7.7).

An attempt was made to detect the anion (35Cl·40Ar)$^{-}$ as well under the conditions just described ($q_{2} = 0.165$ in the collision cell and following segment), but the results were obscured by a small vacuum leak at the AMS high energy magnet. All that can be said at present is that ClAr$^{-}$/Cl$^{-} < 0.1$ in the ISA for the conditions described in the last paragraph. Lenzer et al. (1999) have reported the anion potential well depth to be 64.9 ± 0.6 meV using a zero electron kinetic energy (ZEKE) study, and summarize the results of other studies which range from 58.8 – 103.7 meV. Distelrath and Boesl (2000) have determined a rather large electron affinity, 3.65941 ± 0.00022 eV, larger than that of Cl, also by ZEKE, while Lenzer et al. (1999) have determined a value of 3.66370 ± 0.00026 eV.

Such compound formation may explain the slight but steady Cl$^{-}$ transmission decrease observed at higher cell pressures in Figure 10-1 where the anions were likely cooled, if decreases were not simply due to tuning and ion losses in the high energy regions of the system (see section 10.1.2). For a lab frame kinetic energy < 0.2 eV, there would only be $K_{R} = 70$ meV available for dissociation for ($^{35}\text{Cl}^{40}\text{Ar})^{-}$ incident on $^{40}\text{Ar}$. Such a slope has been observed under similar conditions for other measurements and a more sensitive analysis of the ClAr$^{-}$ signal may be useful in the future.
A detailed scan injecting 380 nA $^{35}$Cl$^{-}$ (FC2) into the ISA and using the AMS system (typical settings, section 7.6) for $^{35}$Cl$^{+3}$ identification at FC7 to search for $^{35}$Cl$^{-}$ + NO$_2$ $\rightarrow$ $^{35}$Cl$^{16}$O$^{-}$, showed very low levels of oxide production with $\Delta V_{ISAS} = 6.7$ V. The ion source was set to $V_s = -20.6960$ V (Keithley reading) and a Nb + (NaCl + S) (3:1 vol) target was used, consistent with the source conditions for Figure 10-1. Results are shown in Figure 10-2 and ISA.
settings in Table 10.1 (q_z = 0.25 for ClO\textsuperscript{−} in the collision cell and following segment). The ionization detector showed a single, sharp peak at q = +3 (see also section 10.3.2).

The overall Cl\textsuperscript{−} attenuation is larger above 1 mTorr cell pressure than that in Figure 10-1, and a comparison is given in the top right-hand panel of Figure 10-2. The expected NO\textsubscript{2} gas NO\textsubscript{2}/N\textsubscript{2}O\textsubscript{4} molecular ratio has been addressed in section 7.5.1 and should be > 99.994\% NO\textsubscript{2} at 6 mTorr and > 99.999\% NO\textsubscript{2} at 1 mTorr at room temperature (~ 300 K). Although ion source and gas conditions were very nearly identical for both measurements, ΔVISAS was not.

For Figure 10-1, ΔVISAS = 5.1 eV giving K_R = 2.95 eV (Eq 6.20), while for Figure 10-2, ΔVISAS = 6.7 eV giving K_R = 3.88 eV. Using bond dissociation energies and electron affinities, Δ_b(Cl\textsuperscript{−} + NO\textsubscript{2} → ClO\textsuperscript{−} + NO) = 1.73 eV, suggesting there was enough kinetic energy available to open the reaction channel in both cases. However, from the electron affinities, EA(NO\textsubscript{2}) = 2.27 eV and EA(Cl) = 3.61 eV, electron transfer and detachment would be energetically favourable with K_R = 3.88 eV only and this may account for the extra Cl\textsuperscript{−} losses with ΔVISAS = 6.7 eV.

Production of ClO\textsuperscript{−} will be discussed below. Unfortunately no detailed scans were taken for Cl\textsuperscript{−} + NO\textsubscript{2} → NO\textsubscript{2}\textsuperscript{−}, (Cl·NO\textsubscript{2})\textsuperscript{−} or other NO\textsubscript{2} reaction products. A rough scan using the 45\textdegree electric analyzer with FC5 (not suppressed) to search for Cl\textsuperscript{−} + NO\textsubscript{2} anion products up to a cell pressure of 3 mTorr NO\textsubscript{2} with ΔVISAS = 10 V and V_s = -20 kV did not indicate large enough levels of reaction products to account for the large initial Cl\textsuperscript{−} losses during experiments with NO\textsubscript{2}. However, there was indication of some NO\textsubscript{2}\textsuperscript{−} production at < 5\% the Cl\textsuperscript{−} beam intensity. More careful measurements would be interesting for future work.

Some amount of electron transfer and detachment is expected for ΔVISAS > 5 eV due to the energy spread of the Cl\textsuperscript{−} beam (see section 10.3.6). However, Lifshitz et al. (1970) measured very low electron transfer cross sections of < 2 x 10\textsuperscript{−18} cm\textsuperscript{2} for K_R < 11 eV (they call this ‘centre of mass energy’), and 1.2 x 10\textsuperscript{−17} cm\textsuperscript{2} for K_R = 30 eV, indicating that this should be a small branching channel for Cl\textsuperscript{−} loss. There may then be further NO\textsubscript{2}\textsuperscript{−} + NO\textsubscript{2} reactions at higher cell pressures. For example, using a flowing afterglow system, Fehsenfeld et al. (1969) have measured a relatively low rate constant for NO\textsubscript{2}\textsuperscript{−} + NO\textsubscript{2} → NO\textsubscript{3}\textsuperscript{−} + NO of 4 x 10\textsuperscript{−12} cm\textsuperscript{3}/s.

The ClO\textsuperscript{−} yield in Figure 10-2 (corrected for stripping, section 7.7) is more than 2 orders of magnitude below the Cl\textsuperscript{−} signal and has a maximum around 0.5 mTorr NO\textsubscript{2} collision cell pressure. Based on the hard sphere approximation with Ar and Cl, the expected number of collisions at this pressure is 1, and at 1 mTorr would be 2 (see Figure 9-2). The collision cross section should be larger in NO\textsubscript{2} than Ar, but the molecule likely needs to be in a favourable
orientation for the reaction to proceed. Given the mass of NO$_2$, the $K_0$ used (related to $\Delta V_{\text{ISAS}}$) and the relatively large Cl$^-$ transmission, it is likely that the Cl$^-$ kinetic energy would drop below the required threshold energy if the reaction did not proceed within the first 2–4 collisions.

On the other hand, the electron affinities are $\text{EA(ClO)} = 2.275$ eV and $\text{EA(NO}_2) = 2.273$ eV so that electron transfer would appear resonant, possibly explaining the subsequent decline in ClO$^-$. Above 1 mTorr, the expected number of collisions is $> 2$ and ClO$^-$ would lose its electron as it reacted with NO$_2$. Furthermore, the kinetic energy of the ClO$^-$ reaction product will already be less than that of the incident Cl$^-$ during the oxygen transfer reaction because of the increase in mass. There is then a steady decline in ClO$^-$ as the neutrals are lost from the cell, but an increase in NO$_2^-$ due to the ClO$^-$ reaction.

However, at even larger pressures the ClO$^-$ curve appears to plateau. This could be indication of an equilibrium condition in the collision cell where kinetic energies are low enough for formation of a (Cl·NO$_2$)$^-$ complex or an adduct that has a dissociation channel to ClO$^-$ and another to NO$_2^-$ on further collisions or has a half-life. The ClO–NO$_2$ bond dissociation energy is given as $111.8 \pm 2.1$ kJ/mol (1.157 eV) and Cl–ONO$_2$ as $172.0$ kJ/mol (1.783 eV) in Haynes and Lide (2011 p. 9-75, 9-76). A measurement of the ClO$^-$ to NO$_2^-$ and NO$_3^-$ ratios over the entire pressure range and with other $\Delta V_{\text{ISAS}}$ would help answer these questions.

### 10.1.2 Losses from Residual Gas

An attempt was made to assess Cl$^-$ losses due to residual gas in the ISA chamber, which can reach $> 2 \times 10^{-5}$ Torr pressure with $> 2$ mTorr collision cell pressure. The ISA chamber cryo-pump was closed and the chamber pressure allowed to rise while the Cl$^-$ current was measured at FC4 (not suppressed). Tuning settings were similar to Table 10.1 for Figure 10-1 at base pressure and $\Delta V_{\text{ISAS}} = 9.8 \pm 0.3$ V. Measurements indicated that attenuation was 10% for chamber pressures in the range $0.5 – 1 \times 10^{-5}$ Torr, and between 20 – 30% for $2 – 5 \times 10^{-5}$ Torr.

These measurements are consistent with the likely number of collisions that occur in the test bed system between high energy (several keV) ions and residual gas during experiments at collision cell pressures above 5 mTorr. For Cl on Ar, the hard sphere approximation with $\sigma_{\text{HS}}$ (Eq 6.28) and the Van der Waals radii in Table 9.3 can be used to calculate the expected number of collisions, $x$, at pressure $P$ over a distance $l$, $<x(P,l)> = \sum x \cdot P_c(x,P,l)$, with $P_c(x,P,l)$ given by Eq 6.34. The chamber before the ISA ($l = 900$ mm) is typically 1 order of magnitude lower in pressure than the ISA chamber.
Setting $P = 2 \times 10^{-5}$ Torr over a distance of $l = 1000$ mm, $<x> = 0.27$. The probability for a single collision over 500 mm (the length of the ISA ‘dead region’ following re-acceleration, see section 7.4) is 0.12, and is 0.02 over $l = 900$ mm at $2 \times 10^{-6}$ Torr. All together, a loss of between 10 and 30% is not unreasonable to expect due to high kinetic energy ion-residual gas collisions in the ISA dead region, deceleration and re-acceleration regions and in the chambers before and after the ISA during gas experiments. Better differential pumping should improve transmission noticeably.

### 10.2 S$^-$ + CH$_4$, Ar, N$_2$O, NO$_2$ and O$_2$: General Transmission

Several gases were surveyed to determine optimum cooling and reaction gases for S$^-$ attenuation and Cl$^-$ transmission. The impetus for NO$_2$ as a reaction gas has been discussed in the introduction to this chapter. In work with cations, N$_2$O is often used as an oxygen donor (see section 9.1 for properties). Because the O is bound very strongly for both SO and SO$_2$ (> 5 eV) and relatively weakly to N$_2$O (< 2 eV), and the electron affinities (EA) of SO and SO$_2$ are both > 1 eV versus -0.03 eV for N$_2$O (Haynes and Lide 2011), N$_2$O was tested for O transfer reactions of the form $S^- + N_2O \rightarrow SO_x^- + N_2$. On the other hand, because the O$_2$ molecule is bound very strongly but still slightly more weakly than the SO$_x$ bonds, and EA(O$_2$) = 0.450 eV (ibid), O$_2$ was tested for O reactions and cooling. Both CH$_4$ and Ar were tested for transmission as potential cooling gases. Further SO$^-$ work was done mainly as a follow-up to the S$^-$ studies, discussed later in this section.

### Table 10.2: Representative ISA Settings for S$^-$ Attenuation Studies

<table>
<thead>
<tr>
<th>Base Pressure</th>
<th>Cy1</th>
<th>Co1</th>
<th>RFQ1 DC</th>
<th>L1</th>
<th>RFQ2 DC</th>
<th>L2</th>
<th>RFQ3 DC</th>
<th>L3</th>
<th>RFQ4 DC</th>
<th>L4</th>
<th>Co2</th>
<th>Cy2</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.6 mTorr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1691</td>
<td>1610</td>
<td>46</td>
<td>23</td>
<td>10</td>
<td>100</td>
<td>-2</td>
<td>100</td>
<td>25</td>
<td>1600</td>
<td>1690</td>
<td></td>
<td></td>
</tr>
<tr>
<td>370 (q$_2 = 0.190$)</td>
<td>30</td>
<td>10</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.6 mTorr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1691</td>
<td>1610</td>
<td>46</td>
<td>23</td>
<td>10</td>
<td>200</td>
<td>0</td>
<td>200</td>
<td>20</td>
<td>1600</td>
<td>1690</td>
<td></td>
<td></td>
</tr>
<tr>
<td>350 (q$_2 = 0.179$)</td>
<td>30</td>
<td>15</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Transmission is given for S⁻ in various gases with $\Delta V_{\text{ISAS}} = 5 – 6.6$ V, using typical AMS settings (section 7.6) for $^{32}\text{S}^- \rightarrow ^{32}\text{S}^+$ detection. See Table 10.2 for representative ISA settings and Table 10.3 for other relevant data such as $\Delta V_{\text{ISAS}}$ and target material: Set A for CH₄, Set B for NO₂, Set C–a for Ar and N₂O.
Table 10.3: Sputter, Kinetic Energy and Transmission Data for S\(^-\) and SO\(^-\) on Ar, CH\(_4\), N\(_2\)O, NO\(_2\) and O\(_2\)

<table>
<thead>
<tr>
<th>Set</th>
<th>Sputter Target Material (ratio by volume) and Ion Source Voltage ([V_s, \text{kV}])</th>
<th>Anion</th>
<th>Gas</th>
<th>(\Delta V_{\text{ISAS}}) [V]</th>
<th>(K_R) [eV]</th>
<th>FC2 [nA]</th>
<th>Base Pisa (x 10(^{-7}) Torr)</th>
<th>FC7 / FC2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>(NaCl + S) + Nb (1:3 vol) (V_s = -20.6952)</td>
<td>(^{32}\text{S})(^-)</td>
<td>CH(_4)</td>
<td>5.1</td>
<td>1.70</td>
<td>3.6</td>
<td>1.2</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NO(_2)</td>
<td>4.5</td>
<td>2.65</td>
<td>17</td>
<td>1.1</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>CuSO(_4) + Ag (1:3 vol) (V_s = -20.0017)</td>
<td>(^{32}\text{S})(^-)</td>
<td>NO(_2)</td>
<td>5.8</td>
<td>3.42</td>
<td>3.1</td>
<td>1.1</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(^{32}\text{S}^{16}\text{O})(^-)</td>
<td>NO(_2)</td>
<td>5.2</td>
<td>2.54</td>
<td>10.25</td>
<td>1.1</td>
<td>12.2*</td>
</tr>
<tr>
<td>C</td>
<td>CuSO(_4) + NaCl + ZnO + Nb (1:1:2:5 vol) (V_s = -20.0097)</td>
<td>a) (^{32}\text{S})(^-)</td>
<td>Ar</td>
<td>6.6</td>
<td>3.67</td>
<td>7</td>
<td>1.6</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b) (^{32}\text{S})(^-)</td>
<td>Ar</td>
<td>4.8</td>
<td>2.67</td>
<td>5.2</td>
<td>2.1</td>
<td>14.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>a) (^{32}\text{S})(^-)</td>
<td>N(_2)O</td>
<td>6.6</td>
<td>3.82</td>
<td>5.2</td>
<td>1.7</td>
<td>11.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b) (^{32}\text{S})(^-)</td>
<td>N(_2)O</td>
<td>6.3</td>
<td>3.65</td>
<td>4.7</td>
<td>2.6</td>
<td>13.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>a) (^{32}\text{S})(^-)</td>
<td>NO(_2)</td>
<td>6.6</td>
<td>3.82</td>
<td>5.2</td>
<td>2.4</td>
<td>11.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b) (^{32}\text{S})(^-)</td>
<td>NO(_2)</td>
<td>6.3</td>
<td>3.72</td>
<td>4.6</td>
<td>2.6</td>
<td>10.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(^{32}\text{S})(^-)</td>
<td>O(_2)</td>
<td>4.8</td>
<td>2.40</td>
<td>5.2</td>
<td>2.1</td>
<td>14.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(^{32}\text{S}^{16}\text{O})(^-)</td>
<td>Ar</td>
<td>6.2</td>
<td>2.82</td>
<td>0.120</td>
<td>2.6</td>
<td>19.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(^{32}\text{S}^{16}\text{O})(^-)</td>
<td>NO(_2)</td>
<td>6.3</td>
<td>3.08</td>
<td>0.120</td>
<td>2.6</td>
<td>17.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(^{32}\text{S}^{16}\text{O})(^-)</td>
<td>O(_2)</td>
<td>6.3</td>
<td>2.52</td>
<td>0.120</td>
<td>2.6</td>
<td>19.0</td>
</tr>
</tbody>
</table>

* Detection was \(X^- \rightarrow ^{32}\text{S}^{2+}\) and \(^{16}\text{O}^{+1}\) through the AMS system. Otherwise, measurement was made monitoring \(X^- \rightarrow ^{32}\text{S}^{3+}\) through the AMS system. Base FC7/FC2 gives the transmission from FC2 before the ISA to the final AMS detector, FC7, at base pressure and is corrected for the cation charge state. CuSO\(_4\) and ZnO were used to promote oxide anion formation. Both Nb and Ag were used to stabilize sputter currents.
Transmission of $^{32}\text{S}^-$ in CH$_4$, Ar, N$_2$O, NO$_2$ and O$_2$ with $\Delta V_{\text{ISAS}}$ in the range 5 V to 6.6 V is shown in Figure 10-3 with some typical ISA settings in Table 10.2 and other relevant data, such as $\Delta V_{\text{ISAS}}$ and sputter target materials, listed in Table 10.3 (correspondence given in the caption for Figure 10-3). For NO$_2$ work, because of the large $S^-$ attenuation, ISA tuning was done in Ar, but tuning for all other gases was done with the gases themselves. The full AMS system was used for all measurements with typical settings (section 7.6) for $^{32}\text{S}^- \rightarrow ^{32}\text{S}^+3$.

Clearly under these conditions, compared to the other gases used, NO$_2$ is far and away the most effective gas for $S^-$ suppression and CH$_4$ for $S^-$ transmission. The relative $S^-$ attenuation in NO$_2$ and CH$_4$ at 6 mTorr pressure was $2 \times 10^{-6}$. From Figure 10-1, the relative attenuation between $S^-$ and Cl$^-$ at 6 mTorr NO$_2$ cell pressure is on the order of $2 \times 10^{-6}$ for this range of $\Delta V_{\text{ISAS}}$, indicating that under these conditions NO$_2$ can be an effective reaction gas for $^{36}\text{S}^-$ attenuation during $^{36}\text{Cl}^-$ measurements.

On the other hand, N$_2$O and O$_2$ did not result in very large $S^-$ attenuations. Even though $K_R$ was less in O$_2$ under the experimental conditions, the $S^-$ transmission was half that of N$_2$O and Ar at 6 mTorr pressure, while transmission was very similar in N$_2$O and Ar at 20%. The rate of loss in transmission through Ar showed signs of decreasing and plateauing at higher pressures, while both N$_2$O and O$_2$ transmission appeared to produce a steady decrease in transmission, albeit at a lower rate than during the initial collisions.

### 10.3 $S^-$ and SO$^- +$ Ar, N$_2$O, NO$_2$ and O$_2$

Figure 10-4 shows terminal voltage scans (‘VT scans’, described in section 7.7, both raw and stripping yield corrected data shown) of $S^-$ and the SY$^-$ reaction products, where Y may be more than one atom, from interaction with N$_2$O, NO$_2$ and O$_2$ in the ISA using Set C–b (see Table 10.3) for each gas respectively. Briefly, the AMS system was tuned for $^{32}\text{S}^- \rightarrow ^{32}\text{S}^+3$ detection with typical settings (section 7.6) except the accelerator terminal voltage was set to $V_T = 1.608$ MV so that a larger parent molecule mass range could be scanned. By scanning $V_T$, leaving the rest of the AMS system tuned for $m/q = 32/3$, the parent anion mass, M, could be calculated from the $V_T$ at which the $^{32}\text{S}^+3$ fragment was detected. The actual composition of the parent molecule was then confirmed by adjusting the AMS settings to detect the other fragments. This will be discussed in more detail for the case of SNO$_2^-$ identification in section 10.3.2.

Pressures for the $V_T$ scans were set at values where significant levels of anion products could be detected. Based on the hard sphere Cl on Ar calculated number of collisions, at 1 mTorr
gas pressure, 2 collisions on average are expected while at 4 mTorr, 8 collisions are expected on average (see Figure 9-2). The numbers are likely larger for the molecular gases used.

In N₂O and NO₂ at 1 mTorr, SN⁻, SOₓ⁻ and SNOₓ⁻ (see 10.3.2 regarding SNO₂⁻) anion products were all observed at 0.1 ppt to several percent levels compared to the S⁻ signal, accounting for only a small portion of the S⁻ attenuations observed in Figure 10-3. Attenuation of the reaction product signal due to ISA tuning should not be more than 5% for SO⁻ and SN⁻, 10% for SNO⁻ and SO₂⁻, and 15% for SNO₂⁻ (see section 10.3.1). Unfortunately these analyses were limited to SY⁻ products alone because of a machine failure and then funding and time limitations. Some data was taken for S⁻ + NO₂ → NO₂⁻, which is the dominant reaction channel for that combination, and will be discussed in section 10.3.5 on S⁻ + NO₂.

In O₂, only SOₓ⁻ products were observed in the range of masses that could be scanned, as would be expected, except for a small NS⁻ peak. The O₂ used has a specification of ≤ 1 ppm hydrocarbon content and was purchased in 1996 whereas measurements were made in 2010. The level of SN⁻ observed in the V_T scan is 0.7 ppm of the S⁻ signal, on the order of the quoted hydrocarbon impurities. Other impurities such as N₂ or NOₓ compounds at similar levels to the hydrocarbon impurities could give rise to such a signal, however the absence of an NSO⁻ peak suggests that the contaminant is likely N₂. This could be considered the first (and likely final) application of RFQ–AMS for gas impurity analysis by anion reaction.

Caption for Figure 10-4

Results are shown for ‘V_T scans’ (section 7.7, detecting ³²S⁺³ fragments after stripping) to examine ³²S⁻ reaction products in 3 gases (Sets C–b in Table 10.3, ΔV_{ISAS} = 4.8 – 6.3 V) and at ISA base pressure with no gas leaked into the collision cell. Gas pressures were set at levels where reasonable levels of reaction products could be detected. Accelerator terminal voltages, V_T, have been converted into parent molecule mass, M, using Eq 7.3 and 7.4 with V_T = 1.608 MV for ³²S⁻ → ³²S⁺³, and data is normalized to the ³²S⁻ → ³²S⁺³ signal (see the following sections for reaction products versus gas pressure plots). The linear and polynomial stripping yield corrections have been discussed in section 7.7 and are shown in each figure with the uncorrected data for comparison. Besides V_T, typical settings (section 7.6) were used and representative ISA settings are given in Table 10.2. In the O₂ product spectron, SN⁻ was produced from O₂ gas contaminants.
Figure 10-4: Scan of the $^{32}\text{S}^-$ Reaction Products from $^{32}\text{S}^- + \text{N}_2\text{O}$, $\text{NO}_2$ and $\text{O}_2$ with $\Delta V_{\text{ISAS}} = 4.8$ V to 6.3 V using the full AMS System to Detect the $^{32}\text{S}^{+3}$ Fragment after Stripping (caption on p. 10—165)
10.3.1 A Note on Reaction Product Transmissions with Reactant ISA Tuning

Typical ISA tuning settings were similar to those in Table 10.2 for most $S^-$ experiments described in this chapter. A low $q_2$ value was used in the collision cell and following segment, on the order of 0.110 for $^{32}S^-$. This would mean that $q_2 = 0.045$ for the most massive anion studied, $(^{32}S^{14}N^{16}O_2)^-$. Trajectory amplitudes increase as $q_2$ decreases from 0.3, as discussed in chapter 5. However, the resultant molecule should be effectively cooler than the initial anion for the reactions studied, at least because of the increase in mass. For example, for larger kinetic energy collisions where the initial kinetic energy of gas constituents can reasonably be neglected, the original $S^-$ kinetic energy would decrease by at least 40% in the formation of $SNO_2^-$. Resultant trajectory amplitudes at higher energies will generally be less than the original, and not larger.

Transmission of $SO^-$ at base pressure (un-cooled) using the ISA settings for $S^-$ was within 5% of the optimized $SO^-$ transmission, and transmission of $SO_2^-$ was within 10% of the optimized $SO_2^-$ transmission. A full calibration for all the molecular anions was not conducted, and the quoted results were for un-cooled anions. However, plotting the transmission loss vs. mass and extrapolating to $m = 78$ amu suggests that the losses from tuning would be within 15% of the optimized tuning transmission at $m = 78$ amu if losses increased linearly with mass. This is an upper limit as the effective loss of kinetic energy due to the increase in mass upon molecular formation, and loss through momentum transfer during the interaction, should improve transmission. Furthermore, the more massive molecular products should suffer less scattering losses than the original anion, and the lower $q_2$ value associated with the larger mass results in less rf heating (Eq 4.42).

10.3.2 Molecular Identification from Stripping Fragments and $NSO_2^-$

A review of the historical difficulties and controversies in identifying the $NSO_2^-$ anion is given in Morgon et al. (1995), who calculated 3.76 eV as the electron affinity for the $NSO_2^\bullet$ radical. Chemical identification proved difficult, and spectroscopic studies were controversial due to similarities with $NSO^-$ spectra.

With AMS by tandem accelerators, molecules can be identified by detecting the fragments after electron stripping in the accelerator high voltage terminal. After a coulomb explosion that can result from stripping in the accelerator, there will be a distribution of final charge states for the resulting fragments. Suppose the parent anion had the form $XY_2^-$ with the
masses of X and Y respectively $m_x \neq m_y$, and there were no background signal contamination. Let $q_x$ and $q_y$ (integers) represent charge states for X and Y respectively.

- If the high energy side of the AMS system were then tuned for $m_x/q_x$ such that $m_y/q_y \neq m_x/q_x$ for all $q_y$ then only 1 peak would be seen in the ionization detector spectrum corresponding to the channel for $q_x$.

- If the high energy side of the AMS system were set for $m_y/q_y$ such that $m_x/q_x \neq m_y/q_y$ for all $q_x$, then two peaks would be seen. The first would correspond to one cation with $m_y/q_y$ entering the ionization detector and would be seen at the channel for charge state $q_y$. The second peak would appear in the spectrum region of $2q_y$ because there is a finite probability that both Y atoms would end up in the charge state $q_y$ and traverse the rest of the system simultaneously, depositing twice the energy of a single $Y^{+q_y}$ cation in the ionization detector. There should normally be lower probability for the double coincidence so that the double coincidence peak would normally be expected to be smaller than the single ion peak (see also Figure 10-11).

- If $m_x = am_y$ ($1 < a$ an integer), then both X and Y fragments could be detected simultaneously by using charge state $q_x = na$ ($n$ also an integer), and tuning for $m_x/q_x = m_y/n$. For simplicity, let $a = 2$ and $n = 1$. The first peak in the spectrum would be for $Y^+$. The second would be for $X^{+2}$ and $2(Y^{+1})$ (see previous bullet). The third would be for $X^{+2} + Y^{+1}$ (both fragments simultaneously produced from stripping). The fourth would be for $X^{+2} + 2(Y^{+1})$. Furthermore, if the cation energies were below the Bragg peak then the $X^{+2}$ and $2(Y^+)$ peaks may also be resolved by the ionization detector window as there would be different amounts of energy loss while passing through it. The 2 $Y^+$ cations would loose twice the energy of a single $Y^+$ cation.

During a $V_T$ scan (section 7.7) for $^{32}S^- + NO_2$ (ISA) $\rightarrow$ $^{32}SY^-$ (AMS) $\rightarrow$ $^{32}S^{+3}$, a peak was observed corresponding to a parent anion molecule $SY^-$ having mass $M = 78$ amu, as would be for $^{14}N^{32}S^{16}O_2^-$. The ionization detector showed a single peak (for $q = +3$) so that a parent molecule containing $2 \times ^{32}S$ could be ruled out. In order to confirm that the parent was indeed composed of $^{32}S$, $^{14}N$ and $2 \times ^{16}O$, the AMS system was then set up for detection of $^{14}N^{+2}$ (which showed a single peak corresponding to $q = +2$), and $^{32}S^{+2}$ which also corresponds to $^{16}O^+$. A
channel spectrum from the ionization detector with the AMS system set for m/q = 32/2 (16/1) is shown in Figure 10-5.

This particular spectrum was taken using typical settings (section 7.6) for Set B (Table 10.3) with 9 mTorr NO₂ and ISA settings as in Table 10.2. The spectrum was re-confirmed during the V_T scans for Figure 10-4.

**Figure 10-5: Ionization Detector Channel Spectrum for NSO₂⁻ \( \rightarrow ^{32}\text{S}^{+2} / ^{16}\text{O}^{+1} \)**

Data were taken with the ISA at 9 mTorr NO₂ injecting \(^{32}\text{S}^-\) (Set B, Table 10.3) and ISA tuning similar to Table 10.2. Typical settings (section 7.6, V_T = 1.75 MV) were used for fragments of m/q = 32/2 (16/1) from a parent mass 78 amu anion. The ionization detector spectrum is consistent with an NSO₂⁻ parent molecular anion.

As described in the 3rd bullet above, the q = +2 peaks for \(2(^{16}\text{O}^+)\) and \(^{32}\text{S}^{+2}\) were separated because the \(^{16}\text{O}^+\) ions lost more energy in the detector window and gas than the \(^{32}\text{S}^{+2}\) ions. This condition applies for ions with energies below the Bragg peak, and further confirms that the peaks were due to both S and O. With this spectrum and observation of the single \(^{32}\text{S}^{+3}\) and \(^{14}\text{N}^{+2}\) peaks it was confirmed that a molecule containing S, N and 2 x O was observed. However, the structural form of the molecule remains ambiguous. Was this an \((\text{S}^- \cdot \text{NO}_2)\) adduct or indeed the NSO₂⁻ molecular anion? If it were an adduct then it would seem reasonably strongly bound as the average gradient along the ground–high voltage terminal section of the accelerator would have been ~ 6.3 kV/cm. This is discussed more in section 10.3.5.2. This technique was also used to confirm the SN⁻, SNO⁻ and SOx⁻ peaks identified in Figure 10-4.
10.3.3 S− and SO− + N₂O

The major anion reaction products from $^{32}\text{S}^-$ + N₂O that contained an S atom, within the range of masses that could be scanned, were NS− and SO−, which appeared in nearly equal proportions in Figure 10-4. Anion adducts with N₂O were not observed. First order estimates calculated from bond dissociation energies, heats of formation and electron affinities for the threshold energy, $\Delta_b$ (see Eq 6.35), for several reactions are listed in Table 10.4. The O transfer reaction would appear exothermic while the N transfer channel endothermic.

A scan of reaction products vs. N₂O pressure using Set C–a (Table 10.3), ISA settings similar to those in Table 10.2 and typical settings (section 7.6) for $^{32}\text{SY}^- \rightarrow ^{32}\text{S}^+3$ detection at FC7 is shown in Figure 10-6. Both NS− and SO− appear to have had similar appearance rates, with that of NS− slightly larger than SO− at lower pressures. The reactions appear to be zero order up to 1 mTorr, but there is onset of a plateau at 2 mTorr even though there is still plenty of S− and N₂O for the reactions to proceed. These products accounted for less than 1% of the S− losses up to 2 mTorr, yet at the onset of the SN− and SO− appearance plateaus, the S− loss rate also changed by decreasing. There were 2 apparent attenuation slopes for S− in N₂O under these conditions in the ISA over the full range of pressures used.

Initially, based on $\Delta V_{\text{ISAS}} = 6.6$, there is enough energy for the NS− reaction to proceed: $K_R = 3.82$ eV (Table 10.3) so that there is an excess of $T_c = K_R - \Delta_b = 2.79$ eV (see Eq 6.35). From Figure 9-2 for Cl on Ar in the hard sphere approximation, 4 collisions may be expected to have occurred on average by 2 mTorr. Moreover, Cl atoms with kinetic energy $K_0 = 5$ eV (lab frame) in the hard sphere ‘free drift’ approximation can be expected to be mostly cooled by 5 collisions (Figure 9-4). This is a reasonable proxy for estimating the kinetic energy of S− on N₂O with the $\Delta V_{\text{ISAS}}$ used. It would suggest that by 2 mTorr, the S− ions that had not reacted to produce NS− were cooled below the required threshold energy for the reaction to proceed. Up to 1 mTorr, between 1 and 2 collisions can be expected to have occurred on average, some leading to reaction. Between 1 – 2 mTorr, more and more of the ion population is cooled, and more and more S− ions do not have enough kinetic energy for the reaction to proceed. Finally, after 2 mTorr the ions are mostly cooled and below the threshold kinetic energy for the $S^- + N_2O \rightarrow NS^- +$ products reaction to proceed. At this point, there would be a plateau representing the reactions that proceeded within the first few collisions, assuming that these ions were not lost to subsequent reactions with further collisions. The electron affinity $E_A(\text{NS}) = 1.194$ eV while
EA(N₂O) < 0 eV so that electron transfer is highly improbable. This could be tested by using different ΔVISAS. Reaction barriers arising from electronic configurations are considered below.

### Table 10.4: Threshold Energy Estimates for Selected S⁻ + N₂O Reactions

<table>
<thead>
<tr>
<th></th>
<th>S⁻ + N₂O</th>
<th>Δb [eV]</th>
<th>S⁻ + N₂O</th>
<th>Δb [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>→ NS⁻ + NO</td>
<td></td>
<td>1.03</td>
<td>→ e + S + N₂O</td>
<td>2.08</td>
</tr>
<tr>
<td>→ NO⁻ + NS</td>
<td></td>
<td>2.19</td>
<td>→ SO⁻ + N₂</td>
<td>−2.68</td>
</tr>
</tbody>
</table>

Δb (see Eq 6.35) provides a first order estimate of the energy required for the reaction to proceed, Δb < 0 eV means the reaction is energetically favourable, Δb > 0 eV means the reaction should be endothermic while Δb = 0 eV means the reaction could be resonant. Values were calculated from bond dissociation energies, heats of formation and electron affinities as compiled in Haynes and Lide (2011).

### Figure 10-6: S⁻ + N₂O Transmission and Reaction Products vs. Pressure at ΔVISAS = 6.6 V

Data was taken using Set C—a (Table 10.3) with ISA tuning similar to Table 10.2 measuring SY⁻ → S⁺³ using typical settings (section 7.6). All data is normalized to the maximum ³²S⁻ + N₂O → ³²S⁺³ transmission at base pressure. Left panel vertical scale is log₁₀ while right panel vertical scales are linear. Not all reactants from Figure 10-4 were monitored.
Conversely, according to the $\Delta_b$ calculations $S^- + N_2O \rightarrow SO^-$ should be exothermic while the data suggests that there is a barrier. After formation, any $SO^- + N_2O$ reactions would likely need to be exothermic given the amount of remaining kinetic energy. The levels of $SO_2^-$ and $NSO^-$ observed in Figure 10-4 were more than 2 orders of magnitude below the $SO^-$ peak suggesting $SO^-$ was not lost through reaction channels to anions containing an S atom.

A survey of the gas phase ion-molecule reaction rate constants compiled by Ikezoe et al. (1987) found 32 listings for reactions with $N_2O$. Of these, only 2 were $> 10^{-9}$ molecule$^{-1}$cm$^3$s$^{-1}$, 4 were between $10^{-9}$ and $10^{-10}$ molecule$^{-1}$cm$^3$s$^{-1}$, and 21 < $10^{-11}$ molecule$^{-1}$cm$^3$s$^{-1}$ (5 reactions were only observed to have taken place), suggesting that $N_2O$ reactions with anions may typically have small cross sections.

Lorquet et al. (1980) explain that there is a barrier to the break-up of $N_2O({}^1\Sigma^+) \rightarrow N_2({}^1\Sigma^+_g) + O({}^3P)$. The initial singlet molecule is linear while the final triplet state is bent and it is the flow of energy into the bending vibrations which provides the driving force for unimolecular dissociation. They calculate an activation energy of ~ 2.34 eV at low pressures and 900 K.

Additional barriers can come from the final electronic state of O and the electronic configuration of $SO^-$. Borin and Ornellas (1999) have described several states for SO. The O in the ground state $N_2O$ molecule corresponds to $O({}^1D)$, not $O({}^3P)$ (Herzberg 1991). There are also barriers due to spin and other quantum number conservations. Armentrout et al. (1982) and Lavrov et al. (2004) have used these arguments to explain reaction barriers for O transfer from $N_2O$ to atomic metal cations, the former suggesting that many of their observed reactions are likely centred on the $N_2O$ singlet-triplet surface crossing.

Similarly, ground state $N_2O$ (${}^1\Sigma$) cannot dissociate to $N$ (${}^4S$) + NO (${}^2\Pi$) in ground states (Herzberg 1991 p. 471) so that there is an additional barrier to N transfer. From this standpoint, both anion reactions discussed have potentially large barriers and should not proceed with ground state $N_2O$ for the pressures and temperatures of ISA operation with low enough kinetic energy $S^-$ anions. An attempt was made to measure the reaction cross sections between base pressure and 1 mTorr cell pressure but cell evacuation times were too long to make multiple measurements feasible within the time available.
10.3.4  $S^-$ and $SO^-$ + $O_2$

Figure 10-7 shows $^{32}S^-$ and $^{32}S^{16}O^- + O_2$ transmissions, and $S^-$, $SO^-$ and $SO_2^-$ reaction product levels vs. $O_2$ pressure with $\Delta V_{\text{ISAS}} = 4.8$ V using Set C (Table 10.3) and typical settings (section 7.6) for $^{32}S^+ \rightarrow ^{32}S^{1+}$ detection at FC7. All $S^- + O_2$ data are normalized to the base pressure $^{32}S^- \rightarrow ^{32}S^{1+}$ signal while SO$^- + O_2$ data is normalized to the base pressure $^{32}S^{16}O^- \rightarrow ^{32}S^{1+}$ signal.

Figure 10-7: $S^-$ and $SO^- + O_2$ Transmission and Reaction Products at $\Delta V_{\text{ISAS}} = 4.8$ V
Table 10.5: Threshold Energy Estimates for Selected S–, SO– and SO2– + O2 Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta_b$ [eV]</th>
<th>Reaction</th>
<th>$\Delta_b$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S^– + O_2 \rightarrow e + S + O_2$</td>
<td>2.08</td>
<td>$S^– + O_2 \rightarrow e + S_2$</td>
<td>1.63</td>
</tr>
<tr>
<td>$\rightarrow SO^– + O$</td>
<td>0.75</td>
<td>$\rightarrow SO_2^–$</td>
<td>–4.95</td>
</tr>
<tr>
<td>$\rightarrow O^– + SO$</td>
<td>0.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$SO^– + O_2 \rightarrow e + S + O_2$</td>
<td>1.13</td>
<td>$SO^– + O_2 \rightarrow S^– + O_3$</td>
<td>3.31</td>
</tr>
<tr>
<td>$\rightarrow O_2^– + SO$</td>
<td>0.68</td>
<td>$\rightarrow O_3^– + S$</td>
<td>3.29</td>
</tr>
<tr>
<td>$\rightarrow SO_2^– + O$</td>
<td>–0.53</td>
<td>$\rightarrow e + S + O_3^–$</td>
<td>5.39</td>
</tr>
<tr>
<td>$\rightarrow O + SO_2$</td>
<td>–0.88</td>
<td>$\rightarrow O_2^– + S + O$</td>
<td>6.04</td>
</tr>
<tr>
<td>$\rightarrow e + SO_3$</td>
<td>–3.03</td>
<td>$\rightarrow O^– + S + O_2$</td>
<td>5.03</td>
</tr>
<tr>
<td>$SO_2^– + O_2 \rightarrow e + SO_3$</td>
<td>1.11</td>
<td>$SO_2^– + O_2 \rightarrow O^– + SO_3$</td>
<td>2.21</td>
</tr>
<tr>
<td>$\rightarrow O_2^– + SO_2$</td>
<td>0.66</td>
<td>$\rightarrow SO^– + O_3$</td>
<td>4.56</td>
</tr>
<tr>
<td>$\rightarrow SO_3^– + O$</td>
<td>0.69</td>
<td>$\rightarrow O_3^– + SO$</td>
<td>3.61</td>
</tr>
</tbody>
</table>

$\Delta_b$ (see Eq 6.35) provides a first order estimate of the energy required for the reaction to proceed, $\Delta_b < 0$ eV means the reaction is energetically favourable, $\Delta_b > 0$ eV means the reaction should be endothermic while $\Delta_b = 0$ eV means the reaction could be resonant. Values were calculated from bond dissociation energies, heats of formation and electron affinities as compiled in Haynes and Lide (2011).

Threshold energy estimates based on bond dissociation energies, heats of formation and electron affinities (as compiled in Haynes and Lide 2011) for several other S–, SO– and SO2– + O2 reactions are given in Table 10.5. Oxygen atom exchange between SOx– and O2 was not considered but could be studied using O isotopes. Of the S– reactions considered, only S– + O2 $\rightarrow$ e + SO2 and SO2– appear exothermic but certainly have barriers associated with bond deformations during formation.

Neutral products were not studied but Fehsenfeld and Ferguson (1969) have measured a low reaction rate constant for S– + O2 $\rightarrow$ e + SO2, 3 x 10–11 molecule$^{-1}$cm$^{3}$s$^{-1}$, which they partially attribute to a barrier associated with bond deformation during the molecular formation.

From Figure 10-7, the SO2– reaction appears either to have been zeroth order with small cross section (see section 10.5), or to have followed from a sequence: S– + O2 $\rightarrow$ SO– + O and
then $SO^- + O_2 \rightarrow SO_2^- + O$. The 2-step sequence was likely the dominant $SO_2^-$ channel as the second step is exothermic and has a 1st order appearance when injecting $SO^-$, as will be discussed below. Furthermore, $SO^-$ production plateaued and eventually showed a loss rate similar to that observed with $SO^-$ when it was directly injected into $O_2$. The subsequent decrease in $S^- + O_2 \rightarrow SO^-$ signal is then from reactions such as $SO^+ + O_2 \rightarrow SO_2^-$, and this explains why $SO_2^-$ production follows $SO^-$ production.

The dominant $S^- + O_2$ reaction observed involving an S containing anion over the mass range scanned was $SO^-$, but showed a very small cross section at $4.5 \times 10^{-17}$ cm$^2$ (section 10.5) over a pressure range where 1 – 2 collisions would be expected on average. From Table 10.5 this reaction appears endothermic, however using $|q|\Delta V_{\text{ISAS}} = 4.8 \text{ eV}$ for $K_0$, $S$ on $O_2$ would have $K_R = 2.4 \text{ eV}$ available for conversion in a reaction, well above the $\Delta b = 0.75 \text{ eV}$ calculated threshold. There would also have been a contribution from $S^-$ anions in the high energy tail of the ion beam energy distribution and > 1% of the ions may have been 10 eV above 4.8 eV (see section 10.3.6). Furthermore, bond deformation barriers may be relatively small as both $O_2$ and $SO$ are linear molecules, although both involve a double bond.

From Figure 10-7 and section 10.5, $SO^-$ had almost twice the overall attenuation cross section of $S^-$ in $O_2$, $1.1 \times 10^{-15}$ cm$^2$ versus $0.66 \times 10^{-15}$ cm$^2$. At low pressure the levels of $S^-$ and $SO_2^-$ reaction products observed while injecting $SO^-$ were very similar. However, the linear plot shows an exponential appearance curve for $SO^- + O_2 \rightarrow SO_2^-$ suggesting this was a 1st order reaction, and the cross section was the largest calculated for this chapter, $1.8 \times 10^{-14}$ cm$^2$ (section 10.5). On the contrary, the $S^-$ appearance was linear on the linear plot and had a very small cross section of $2.8 \times 10^{-17}$ cm$^2$. These two reaction channels will now be considered separately.

From Table 10.5, $SO^- + O_2 \rightarrow SO_2^- + O$ is exothermic. After an initial exponential rise, up to about 0.5 mTorr, above which more than 1 collision may be expected on average, the $SO_2^-$ production rate begins to decrease but the $SO_2^-$ signal continues increasing. None of the $SO_2^- + O_2$ reaction channels in Table 10.5 appear to be exothermic and the reduction in $SO_2^-$ appearance rate may be due to a combination of decreasing $SO^-$ levels and $SO_2^-\cdot O_2$ and $SO^-\cdot O_2$ adduct formation at lower kinetic energy and higher pressure. Finally, at just over 6 mTorr cell pressure the $SO_2^-$ signal matches the $SO^-$ signal suggesting that most of the $SO^-$ reacts with $O_2$ to form $SO_2^-$ during collisions.
Both of the \( \text{SO}^- + \text{O}_2 \rightarrow \text{S}^- \) channels considered in Table 10.5 were endothermic by > 3 eV. For this system with \( \Delta V_{\text{ISAS}} = 4.8 \) V a value of \( K_R = 1.92 \) eV may be used, > 1 eV below the calculated \( \Delta b \) for the reactions considered for \( \text{S}^- \) production. The \( \text{S}^- \) signal peaked at 1 mTorr cell pressure, plateaued, and then decreased with a similar slope to the \( \text{SO}^- \) attenuation curve. Two explanations for this trend are now considered.

First, the \( \text{S}^- \) may be produced in the high energy region between the magnet and ISA from collisions with residual gas. In this scenario, the \( \text{S}^- \) would be left with \( K_0 = 13.3 \) keV kinetic energy in the lab frame. Such anions would be reflected from the deceleration potential of the ISA deck. Neutrals produced in such a fashion may be re-ionized, but the majority would not have the correct kinetic energy for analysis by the AMS system. Dissociative collisions after the ISA re-acceleration stage would likewise result in \( \text{S}^- \) ions with 13.3 keV. Such ions would be filtered out based on kinetic energy after stripping but prior to the final AMS detector.

Second, the ion beam may have had a relatively large high energy tail such that, even after deceleration, many ions had enough energy for the \( \text{SO}^- + \text{O}_2 \rightarrow \text{S}^- \) reaction to proceed during initial collisions. The \( \text{S}^- \) signal is roughly a constant 2 orders of magnitude lower than the \( \text{SO}^- \) signal, meaning that ~ 1% of the anion beam energy spread would need to have been above the required threshold energy after deceleration. In the case of \( \text{SO}^- + \text{O}_2 \rightarrow \text{S}^- + \text{O} + \text{O}_2, K_0 \geq 11 \) eV would be required, 6.3 eV larger than \(|q|\Delta V_{\text{ISAS}} \) and 0.3% larger than 20 keV (ion acceleration from the ion source). In the case of \( \text{SO}^- + \text{O}_2 \rightarrow \text{S}^- + \text{O}_3, K_0 \geq 8.3 \) eV would be required, 3.5 eV larger than \(|q|\Delta V_{\text{ISAS}} \) and 0.2% larger than 20 keV. Such energy spreads are not unreasonable for the ion source conditions and are consistent with measured kinetic energy distributions under similar conditions (see section 10.3.6). Incorporation of a good electric analyzer before the ISA and a well-designed cooling cell before the reaction cell could have removed these ambiguities.

Finally, it should be noted that the ISA inner apertures (L3 and L4) were between 30 V – 50 V. Increasing aperture size and introduction of a cooling cell before the reaction cell should help avoid use of large aperture voltages during reaction studies while maintaining high transmission.

10.3.5 \( \text{S}^- \) and \( \text{SO}^- + \text{NO}_2 \) and \( \text{Ar} \)

Over the course of reaction studies with the ISA, \( \text{NO}_2 \) was found to have a relatively large overall attenuation cross section with anions when the \( \text{NO}_2 \) electron affinity was larger than
the atomic or molecular electron affinity of an anion. Studies used 4 keV Cs+ sputtering and 20 keV total anion acceleration from the ion source (15 keV for some heavier molecular anions, see chapter 12), with 4 V ≤ ΔV_{ISAS} ≤ 12 V typically. However, data consistently showed attenuation plateaus for highly reactive systems. The plateau attenuation levels and onset gas pressures varied with different molecular entities, but were consistent for a given entity.

In the case of S–, the plateau was at 7 orders of magnitude attenuation with onset near 6 mTorr cell pressure whether using the collision cell with gradient bars and φ3 mm apertures or with φ2 mm apertures and without gradient bars. Figure 10-8 compares S– + NO2 attenuation data taken over the course of 4 years with tuning done separately for each set. The attenuation has an average cross section of 6.6 x 10^{-15} cm² over the range of ΔV_{ISAS}, differing from the cross sections of individual curves by < 2% (section 10.5). The results are very consistent but a full understanding of the attenuation plateau remains elusive.

There are a number of possible sources for the plateau, more than one of which are likely responsible. For example, there may be un-reactive S– and NO2 excited states, S– dissociation channels after adduct formation (eg. S•NO2), or S-containing reaction products (eg. SO–) that react further to re-produce S–. Such considerations led to a study of the S– + NO2 reaction products which showed the levels of S– and SO– at higher pressures were rather similar. This led to a study of the S-atom compound anion reaction products from SO– + NO2. Before discussing these studies, measurements related to ‘fast neutral’ S– production will be addressed.

10.3.5.1 Fast Neutral / Ion Contribution to the S– + NO2 Plateau

As discussed for Cl– in Ar (section 10.1.2), a portion of the S– ions will be neutralized by high energy collisions with residual gas between the magnet and ISA chamber. Some of these ‘fast neutrals’ may have an appropriate trajectory to pass through the ISA apertures and be re-ionized through interaction with residual gas, especially in the ‘dead region’ following the re-acceleration stage of the ISA (see section 7.4). Of the ions in the ± 10 mrad restricted beam at the φ2 mm aperture, those within about ± 1.5 mrad could pass the φ3 mm exit apertures of the collision cell. A small fraction of these may be re-ionized by further interaction with NO2. ‘Fast neutrals’ that had been re-ionized between the ISA deceleration and re-acceleration stages and passed all apertures would have kinetic energy K_0 ≥ q(V_s + V_{ISA}) ~ 2qV_s and would not increase background to the 20 keV S– signal measured with the full AMS system.
Data for $^{32}$S$^- +$ NO$_2$ attenuation was taken over the course of 4 years using the ISA with gradient rods and $\phi$3 mm apertures (A–E) and the ISA without gradient bars and $\phi$2 mm apertures (F). Typical settings were used in all cases (section 7.6). Normalization was to the base pressure FC7 signal for each measurement respectively, minimum count rates are shown in the figure. The ion source deck voltage and ISA deck voltage difference is given by $\Delta V_{\text{ISAS}}$ (Eq 7.1, shown in the figure for each curve). With $|q|$ the absolute value of the anion charge, $K_0 = |q|\Delta V_{\text{ISAS}}$ represents a minimum ion axial kinetic energy after full deceleration.

For curves A – D and E, the AMS system was set for $^{32}$S$^- \rightarrow ^{32}$S$^+3$ detection at FC7 using $V_T > 1.6$ MV. The ionization detector showed a clean spectrum with a well-resolved peak on the $q = +3$ channel in each case. Curves A – D have the following correspondences with Table 10.3: A is Set A, B is Set B, C is Set C–a, D is Set C–b. Curve E was measured by $^{32}$S$^- \rightarrow ^{32}$S$^-$ detection at FC7 using $V_T = 1$ MV and the ionization detector showed a clean spectrum with a well-resolved peak on the $q = +1$ channel. Further details are given in section 10.3.5.1 (description of Figure 10-9). Curve F is the $^{32}$S$^-$ attenuation curve from the $^{36}$Cl/Cl = 4.16 x 10$^{-11}$ standard measurement. Transmission FC2 – FC7 was 5% while injecting 30 pA $^{32}$S$^-$. More details can be found in chapter 11. A linear regression was applied to all data points in the plot (from all 6 curves, as if they were 1 data set) from 1 – 2.5 mTorr. The slope was used to find the average cross section measured over this range of $\Delta V_{\text{ISAS}}$ for S$^- +$ NO$_2$ attenuation, 6.6 x 10$^{-15}$ cm$^2$ (Table 10.8), and differed from individual cross sections by < 2%.
Obversely, sputter source ion beams have associated kinetic energy spreads ($\Delta K_0$, axial) and the ISA test bed may have allowed $\Delta K_0 > 180$ eV through the $\phi2$ mm aperture for injection into the ISA (see section 10.3.6). ‘Fast ions’, possibly representing several percent of the beam in the case of atomic anions, may have very different attenuations than slower ions. For example more collisions may be required before substantial levels of adducts are formed or reaction equilibria are reached, and reaction cross sections vary with energy (eg section 6.2).

For anion studies, the ISA deck voltage ($V_{ISA}$) was maintained a few volts higher than the ion source deck voltage ($V_s$) so that ions with axial kinetic energy $qV_s$ ($q$ is the charge) would be decelerated to $|q|\Delta V_{ISAS} = |q|(V_{ISA} – V_s) > 0$ eV (Eq 7.1). In order to study possible plateau contributions from ‘fast neutrals’ and ‘fast ions’, $\Delta V_{ISAS}$ was varied at base cell pressure such that $\Delta V_{ISAS} < 0$ V. Then $S^-$ transmission versus NO$_2$ pressure with $\Delta V_{ISAS} = –257$ V and 5.3 V was measured for comparison.

<table>
<thead>
<tr>
<th>$\Delta V_{ISAS}$ [V]</th>
<th>Final Detector $^{32}$S$^+$ Signal</th>
<th>Normalized Signal</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3</td>
<td>100 pA</td>
<td>1</td>
</tr>
<tr>
<td>–62</td>
<td>48000 c/s</td>
<td>$8 \times 10^{-5}$</td>
</tr>
<tr>
<td>–137</td>
<td>648 c / 100 s</td>
<td>$10^{-8}$</td>
</tr>
<tr>
<td>–227</td>
<td>616 c / 100 s</td>
<td>$10^{-8}$</td>
</tr>
<tr>
<td>–975</td>
<td>549 c / 100 s</td>
<td>$10^{-8}$</td>
</tr>
</tbody>
</table>

“c” is for “counts” and “s” for “seconds”. $\Delta V_{ISAS}$ (Eq 7.1) is the difference between ion source and ISA deck voltages, $\Delta V_{ISAS} = V_s – V_{ISA}$. When $\Delta V_{ISAS} < 0$ only anions with kinetic energy $K_0 > q\Delta V_{ISAS}$ ($q$ is charge) or neutrals will not be reflected during deceleration. Ions were initially accelerated by $V_s = –20.7$ keV and 4.4 nA $^{32}$S$^-$ (at FC2) was injected into the ISA. Typical settings (section 7.6) were used for $^{32}$S$^- \rightarrow ^{32}$S$^+$ in the final AMS detector (FC7 and ionization detectors used). Base ISA cell pressure was $P_{isa} = 1.5 \times 10^{-7}$ Torr. With either FC1 or FC2 in the path of the ions, no signal was observed at FC7 over 300 s for any of the $\Delta V_{ISA}$ used. The Nb + (NaCl + S) (3:1 vol) target was sputtered by 4 keV Cs$^+$.

Table 10.6 shows the results of a ‘$V_{ISA}$ scan’ at base ISA chamber pressure ($P_{isa} = 1.5 \times 10^{-7}$ Torr). A Nb + (NaCl + S) (3:1 vol) was sputtered with $V_s = –20.7$ kV to produce 4.4 nA of $^{32}$S$^-$ (at FC2) for injection into the ISA Typical settings (section 7.6) were used except the accelerator terminal was set at $V_T = 1$ MV for $^{32}$S$^- \rightarrow ^{32}$S$^+$ detection at FC7. The ionization detector spectrum showed a single, sharp peak at the $q = +1$ channel and signals were measured for 100 s with the ionization detector when count rates were below 1000 c/s. Tuning was similar
to Table 10.1 (for Figure 10-2) for Cl\textsuperscript-- in the ISA, and S\textsuperscript-- → \textsuperscript{32}S\textsuperscript{+} transmission FC2 to FC7 was 2.3\% with ΔV\textsubscript{ISA} = 5.3 V.

As V\textsubscript{S} was lowered, ΔV\textsubscript{ISA} became negative and ions were reflected from the ISA chamber. For ΔV\textsubscript{ISA} < −130 V, the drop in current began to plateau at about 6 c/s which represented 10\textsuperscript{−8} of the S\textsuperscript-- current with ΔV\textsubscript{ISA} = 5.3 V which is within the range of typical ΔV\textsubscript{ISA} for the studies discussed in this thesis. Because the beam object was not well defined at FC1, the question may arise as to whether this signal was from a combination of both fast neutrals and a tiny fraction of the high kinetic energy ‘fast ion’ S\textsuperscript-- tail that exceeded K\textsubscript{0} = q(V\textsubscript{S} + ΔV\textsubscript{ISA}) and passed the φ2 mm aperture (see section 10.3.6). No signal was observed at FC7 over 300 s for any of the ΔV\textsubscript{ISA} when either FC1 or FC2 were placed in the path of the ions and there was an apparent gradual and continuous decrease in signal as ΔV\textsubscript{ISA} was lowered.

Tuning was not attempted while lowering V\textsubscript{ISA}. The fringing fields in the acceleration regions of the ISA should not have affected neutrals but would have affected high energy ions. Conversely, between ΔV\textsubscript{ISA} = −230 V and −975 V there was only an 11\% drop in signal. If the beam object were well defined at FC1 then an energy spread of ΔK\textsubscript{0} = 180 eV might be expected after the φ2 mm aperture for injection into the ISA (see section 10.3.6). Even with a poorly defined object, a drop of only 11\% is low if the signal were due to fast S\textsuperscript-- ions rather than re-ionized S ‘fast neutrals’. On the other hand, count rates were on the order of 6 c/s and the statistical uncertainty in the measurements, given that only about 600 c were measured at lower ΔV\textsubscript{ISA}, would be ±25 c. The observed decrease was greater than 25 c and some ambiguity as to the contribution from ‘fast ions’ remains. Narrowing the slits at FC1 could help clarify the results.

Nonetheless, the data indicated that the system was prone to a background from processes unrelated to the collision cell and low energy S\textsuperscript-- + NO\textsubscript{2} interactions, even at base pressure.

Using the same target material with the same source and AMS conditions as just outlined, \textsuperscript{32}S\textsuperscript{−} + NO\textsubscript{2} → \textsuperscript{32}S\textsuperscript{−} → \textsuperscript{32}S\textsuperscript{+} transmission was studied with ΔV\textsubscript{ISA} = 5.3 V and then −227 V. These conditions yielded 75 nA \textsuperscript{37}Cl\textsuperscript{−} (at FC2) which was used with ΔV\textsubscript{ISA} = 5.3 V and NO\textsubscript{2} for ISA tuning while detecting \textsuperscript{37}Cl\textsuperscript{+} at FC7 using VT = 1 MV. At base pressure (P\textsubscript{ISA} = 1.5 x 10\textsuperscript{−7} Torr), 4.6 nA Cl\textsuperscript{−} was detected at FC7 for a transmission FC2 to FC7 of 6.1\%. Similarly, 6 nA of \textsuperscript{32}S\textsuperscript{−} (at FC2) were injected into the ISA and the FC7 signal at base pressure was 330 pA for an FC2 to FC7 transmission of 5.5\%. In both cases, the ionization detector showed a single, sharp peak at the q = +1 channel and no signal was observed at FC7 over 300 s (at 1, 5 and 7 mTorr) when
either FC1 or FC2 were placed in the path of the ions. All $\Delta V_{\text{ISAS}} = -227$ V data were collected using the ionization detector over an accumulation time of 100 s.

After the NO$_2$ scan using $V_T = 1$ MV, the AMS system was re-tuned for $^{32}$S$^- \rightarrow ^{32}$S$^{+3}$ detection with $V_T = 1.75$ MV and the ISA settings for $\geq 7$ mTorr NO$_2$ were re-tuned using the S$^-$ beam and $\Delta V_{\text{ISAS}} = 5.3$ V. The NO$_2$ scan for 7, 8, 9 and 10 mTorr was repeated using $\Delta V_{\text{ISAS}} = 5.3$ V and then $-227$ V, and data normalized to the base pressure $\Delta V_{\text{ISAS}} = 5.3$ V $^{32}$S$^{+3}$ signal at FC7 with an accumulation time of 50 s at each point. The ionization detector showed a single, sharp peak on the $q = +3$ channel. No signal was observed at FC7 over 300 s at 7 mTorr when either FC1 or FC2 were placed in the path of the ions.

Results are shown in Figure 10-9. Both $V_T = 1$ MV and 1.75 MV sets of measurements were consistent. For the S$^- +$ NO$_2$ measurements with $\Delta V_{\text{ISAS}} = 5.3$ V, the plateau onset was again at 6 mTorr and at about $7.5 \times 10^{-7}$ of the original S$^-$ signal. With $\Delta V_{\text{ISAS}} = -227$ V, the signal initially rose with pressure and then plateaued at 1.5 times the base pressure signal at 2 mTorr cell pressure. This pressure range corresponded to 3 orders of magnitude increase in chamber pressure, with the initial pressure of Pisa = $1.5 \times 10^{-7}$ Torr and Pisa = $2.2 \times 10^{-5}$ Torr corresponding to 2 mTorr cell pressure (also see calculations in section 10.1.2).

A small portion of these signals may arise from ionization of gas impurities. After the above measurements, 12 nA of $^{16}$O$^-$ (at FC2, same source conditions) was injected with 6 mTorr NO$_2$ in the cell and the AMS system still set for $^{32}$S$^- \rightarrow ^{32}$S$^{+3}$ at $V_T = 1.75$ MV. With $\Delta V_{\text{ISAS}} = 5.3$ V, 2 trials yielded 601 c and 597 c in 1000 s. Based on an FC2 to FC7 transmission of 5.5%, this represents $1.5 \times 10^{-12}$ of the O$^-$ current, 5 orders of magnitude below the $^{32}$S$^-$ plateau. With $\Delta V_{\text{ISAS}} = -227$ V, 184 c in 1000 s were observed, $7 \times 10^{-13}$ of the O$^-$ current at FC2 assuming 5.5% transmission again. With FC1 lowered into the ion path there was no signal observed at FC7 in 1000 s. Conversely, with the AMS system set for $^{16}$O$^+$ detection and $\Delta V_{\text{ISAS}} = -982$ V, the ionization detector registered $> 1000$ c/s.

All of this suggests that gas impurities likely contributed little to the S$^-$ plateau while ‘fast neutrals’ and ‘fast ions’ may have played a significant role. The S$^-$ signal for $\Delta V_{\text{ISAS}} = -227$ V with $\geq 6$ mTorr NO$_2$ cell pressure when injecting $^{32}$S$^-$ was 25% of that for $\Delta V_{\text{ISAS}} = 5.3$ V. About $1/4$ of the S$^-$ plateau with the current ISA and test bed appears to be due to interactions unrelated to the interactions taking place within the collision cell and at low kinetic energy.
A Nb + (NaCl + S) (3:1 vol) target was sputtered with 4 keV Cs+ and the ion source deck set to –20.7 kV. Data was taken injecting 75 nA \(^{37}\text{Cl}^-\) and 6 nA \(^{32}\text{S}^-\) as measured at FC2. Detection was with the final AMS detector (FC7) using accelerator terminal voltages \(V_T = 1\) MV for stripping to \(q = +1\) and \(V_T = 1.75\) MV for stripping to \(q = +3\). Tuning for ISA settings was initially done with \(^{37}\text{Cl}^-\). After the attenuation measurements using \(V_T = 1\) MV, the higher pressure ISA settings were re-tuned using \(^{32}\text{S}^-\) with \(V_T = 1.75\) MV and several points were re-examined.

The ISA deck \((V_{ISA})\) and ion source deck \((V_s)\) voltage difference is given by \(\Delta V_{ISA}\) (Eq 7.1) When \(\Delta V_{ISA} < 0\) V, ions having axial kinetic energy \(K_0 < q(V_s + \Delta V_{ISA})\) would have been reflected during deceleration in the ISA, where \(q\) is the ion charge. When \(\Delta V_{ISA} \geq 0\) V, ions with initial \(K_0 = qV_s\) would have had \(K_0 = |q|\Delta V_{ISA}\) after full deceleration in the ISA.

Data is normalized to the respective base pressure (Pisa = \(1.5 \times 10^{-7}\) Torr) signals at FC7. All \(S^{+3}\) data, besides base pressure, was collected with a count accumulation time of 50 s. For \(S^{+1}\) with \(\Delta V_{ISA} = -227\) V, an accumulation time of 100 s was used for each point. The measurements at 9 mTorr with \(\Delta V_{ISA} = -227\) V for both \(S^+\) and \(S^{+3}\) are given in the figure.
Background from these types of phenomena can be reduced by designing a system that does not have a straight line of sight between ISA entrance and exit, and incorporating an electric analyzer to reduce the ion beam energy spread injected into the ISA. On the other hand, the Cl\(^-\) and S\(^-\) relative attenuations that were measured using \(V_T = 1\) MV stripping to \(q = +1\) were the same as those measured using \(V_T = 1.75\) MV and stripping to \(q = +3\). Although a proper \(m = 36\) amu background analysis was not done using \(V_T = 1\) MV, the data suggest that \(^{36}\)Cl\(^-\) analysis with \(V_T \leq 1\) MV using the \(q = +1\) charge state after stripping should be possible with rf quadrupole reaction cells and accelerator mass spectrometry (RFQ–AMS).

### 10.3.5.2 S\(^-\) and SO\(^-\) + NO\(_2\) Reactions

Table 10.7 lists some reaction energy threshold estimates calculated (as described in section 6.3) using bond dissociation energies, heats of formation and electron affinities as compiled in Haynes and Lide (2011). There are several reactions that appear to be energetically favourable for S\(^-\), SO\(^-\), SO\(_2\)\(^-\) and NO\(_2\)\(^-\) + NO\(_2\). Electron transfer may be expected to have the largest cross section given the relative range for electron versus atom tunnelling, and the often much smaller geometrical deformations required during electron capture. Excited states and configurations of NO\(_2\) are reviewed in Wilkinson and Whitaker (2010).

Figure 10-10 shows the results of monitoring reactant and product levels for SO\(^-\) and S\(^-\) in NO\(_2\) versus pressure, cross sections are calculated in section 10.5. The top left panel shows the results of injecting \(^{32}\)S\(^{16}\)O\(^-\) while leaking Ar and NO\(_2\) (separately, not mixed) into the ISA with \(\Delta V_{\text{ISAS}} = 6.3\) V using Set C (for both Ar and NO\(_2\), Table 10.3) and typical settings (section 7.6) for \(^{32}\)SY\(^-\) \(\rightarrow^{32}\)S\(^+\)\(^3\) detection using the full AMS system. The top right panel shows results for analyses while injecting \(^{32}\)S\(^-\) (Set C–b for NO\(_2\) with \(\Delta V_{\text{ISAS}} = 6.3\) V, Sets C–a and –b for Ar, Table 10.3).

Representative ISA settings can be found in Table 10.2. Tuning was done with Ar for both SO\(^-\) and S\(^-\), and \(q_2\) varied in the range 0.08 \(\leq q_2 \leq 0.11\) for \(^{32}\)S\(^{16}\)O\(^-\) in the collision cell and following ion guide. All SO\(^-\) data was normalized to the base pressure \(^{32}\)S\(^{16}\)O\(^-\) \(\rightarrow^{32}\)S\(^+\)\(^3\) signal while S\(^-\) data was normalized to the base pressure \(^{32}\)S\(^-\) \(\rightarrow^{32}\)S\(^+\)\(^3\) signal prior to leaking gas for each gas pressure scan respectively. The ionization detector channel spectrum showed 1 well-defined peak at the channel for \(q = +3\) in each case.
### Table 10.7: Threshold Energy Estimates for Selected $S^-$, $SO^-$, $SO_2^-$ and $NO_2^-$ + $NO_2$ Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta_b$ [eV]</th>
<th>Reaction</th>
<th>$\Delta_b$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S^-$ + $NO_2$ to $e + S + NO_2$</td>
<td>2.08</td>
<td>$S^-$ + $NO_2$ to $NS^- + O_2$</td>
<td>0.59</td>
</tr>
<tr>
<td>$NO_2^-$ + S</td>
<td>$-0.20^a$</td>
<td>$O_2^-$ + $NS$</td>
<td>1.34</td>
</tr>
<tr>
<td>$SO^-$ + NO</td>
<td>$-1.24$</td>
<td>$e + NS + O_2$</td>
<td>1.79</td>
</tr>
<tr>
<td>$NO^- + SO$</td>
<td>$-0.14$</td>
<td>$SO_2^- + N$</td>
<td>$-0.39$</td>
</tr>
<tr>
<td>$e + SO + NO$</td>
<td>$-0.12$</td>
<td>$e + SO_2 + N$</td>
<td>0.72</td>
</tr>
<tr>
<td>$SO^- + NO_2$ to $e + SO + NO_2$</td>
<td>1.13</td>
<td>$S^- + NO_3$</td>
<td>2.28</td>
</tr>
<tr>
<td>$NO_2^- + SO$</td>
<td>$-1.15$</td>
<td>$NO_3^- + S$</td>
<td>0.42</td>
</tr>
<tr>
<td>$SO_2^- + NO$</td>
<td>$-2.52$</td>
<td>$O_3^- + S$</td>
<td>3.29</td>
</tr>
<tr>
<td>$NO^- + SO_2$</td>
<td>$-1.44$</td>
<td>$e + SO_2 + NO$</td>
<td>$-1.41$</td>
</tr>
<tr>
<td>$SO_2^- + NO_2$ to $e + SO_2 + NO_2$</td>
<td>1.11</td>
<td>$NO^- + SO_3$</td>
<td>0.64</td>
</tr>
<tr>
<td>$NO_2^- + SO_2$</td>
<td>$-1.12$</td>
<td>$SO^- + NO_3$</td>
<td>3.56</td>
</tr>
<tr>
<td>$SO_3^- + NO$</td>
<td>$-1.30$</td>
<td>$NO_3^- + SO$</td>
<td>0.74</td>
</tr>
</tbody>
</table>

$\Delta_b (NO_2^- + NO_2 \rightarrow NO_3^- + NO) = -0.63^b$ eV

Rate constants a) $k$ (therm) = $1.3 \times 10^{-9}$ cm$^3$/mol.s (Dunkin et al. 1972), $k$ (0.3 eV lab frame) = $8.2 \times 10^{-10}$ cm$^3$/mol.s (Hughes et al. 1973); b) $k = 4 \times 10^{-12}$ cm$^3$/mol.s (Fehsenfeld et al. 1969).

$\Delta_b$ (see Eq 6.35) provides a first order estimate of the energy required for the reaction to proceed, $\Delta_b < 0$ eV means the reaction is energetically favourable, $\Delta_b > 0$ eV means the reaction should be endothermic while $\Delta_b = 0$ eV means the reaction could be resonant. Values were calculated from bond dissociation energies, heats of formation and electron affinities as compiled in Haynes and Lide (2011).

Also shown is $NO_2^-$ production using Set B (Table 10.3) for both $S^-$ ($\Delta V_{ISAS} = 5.8$ V) and $SO^-$ ($\Delta V_{ISAS} = 5.2$ V) with $V_T = 1.75$ MV for $^{16}O^+$ detection. This would be the same AMS tuning as for $^{14}N^{32}S^- \rightarrow ^{32}S+^2$ but, given the relative levels of $NS^-$ and $NO_2^-$ production, $NS^-$ did not represent a significant interference. Ionization detector channel spectra taken at base pressure and 6 mTorr showed 2 well-defined peaks, with that corresponding to $O^+$ larger than that corresponding to $2O^+$ (see section 10.3.2).

Stripping yields for O and S were not calibrated empirically with the IsoTrace system but a stripping correction was approximated. At 1.75 MV there is an effective 0.61 MV available for
$^{14}\text{N}^{16}\text{O}_2^- \rightarrow ^{16}\text{O}^+$ stripping. An efficiency of 52.8% was assumed based on Wittkower and Betz (1973 p. 126) value for the N$^+$ stripping yield in Ar at 0.6 MV. An absolute $^{32}\text{S}^- \rightarrow ^{32}\text{S}^{+2}$ stripping yield was assumed to be 31.5% (see section 7.7) so that the O$^+$ data were multiplied by 0.60.

For $\text{SO}^- + \text{NO}_2 \rightarrow \text{NO}_2^- \rightarrow \text{O}^+$, data were normalized to the base pressure $^{32}\text{S}^{16}\text{O}^- \rightarrow ^{32}\text{S}^{+2}$ signal with $V_T = 1.75$ MV. The ionization detector spectrum showed 3 well-defined peaks, as expected for $^{16}\text{O}^+$, $^{32}\text{S}^{+2}$ and $^{16}\text{O}^+ + ^{32}\text{S}^{+2}$. Wittkower and Betz (1973 p. 139) give the $\text{Cl}^{+2}$ yield at 1 MV as 41.7% and this was used as a proxy for the $\text{S}^{+2}$ yield. Since this was similar to that assumed for $^{14}\text{N}^{16}\text{O}_2^- \rightarrow ^{16}\text{O}^+$ stripping at 1.75 MV, and all stripping yields were based on proxy data, a stripping yield correction was not applied to this data set.

In the future, the SNO$^-$ and SNO$_2^-$ products could be used to calibrate stripping efficiencies for S, N and O.

Cross section and reaction rate coefficient estimates are described in section 10.5. The overall attenuation cross section of SO$^-$ in NO$_2$, $7.1 \times 10^{-15}$ cm$^2$, appears to be slightly larger than for $\text{S}^-$, $6.6 \times 10^{-15}$ cm$^2$, which has a larger electron affinity. Electron transfer to NO$_2$ (expected to be exothermic) was the dominant reaction channel observed for both SO$^-$ and S$^-$, with cross sections $1.2 \times 10^{-15}$ cm$^2$ and $1.0 \times 10^{-15}$ cm$^2$ respectively (section 10.5). The corresponding reaction rate coefficient estimate for $\text{S}^- + \text{NO}_2 \rightarrow \text{NO}_2^-$ is $k = 5.9 \times 10^{-10}$ cm$^3$molecule$^{-1}$s$^{-1}$. While lower than the thermal coefficient given by Dunkin et al. (1973) of $k = 1.3 \times 10^{-9}$ cm$^3$molecule$^{-1}$s$^{-1}$, it is consistent with that of Hughes et al. (1973) given for 0.3 eV lab frame kinetic energy, $k = 8.2 \times 10^{-10}$ cm$^3$molecule$^{-1}$s$^{-1}$.

There is an initial linear rise in NO$_2^-$ with both SO$^-$ and S$^-$, and then an exponential attenuation that almost certainly resulted from NO$_2^-$ + NO$_2$ reactions. The peak NO$_2^-$ levels represented only about 20 – 35% of the S$^-$ and SO$^-$ losses. Unfortunately the ionization detector widow broke before NO$_x^-$ and O$_x^-$ reaction products and (NO$_2)_x^-$ clusters could be scanned, and there was not sufficient time or funding to continue measurements after it was replaced. It is not clear whether the peak NO$_2^-$ levels indicated rapid NO$_2^-$ + NO$_2$ reactions or that other channels were also responsible for significant (> 10%) S$^-$ and SO$^-$ losses.

However, from the Ar data, initial high kinetic energy collisions leading to scattering and electron detachment may account for a substantial portion of the anion losses. This should be less severe in NO$_2$ even though it is more massive than Ar (see sections 9.3 and 9.3.1). Regardless, the Ar data and Figure 9-5 suggest that 50 – 70% attenuation is not an unreasonable figure under the conditions of these measurements.
The second major channel observed for $S^-$ + NO$_2$ was production of SO$^-$ which appears exothermic according to the calculations of Table 10.7. It reached a maximum at about 1% of the initial $S^-$ beam at a pressure where there was likely 1 collision on average with NO$_2$ according to the hard sphere calculations in section 9.2. The SO$_2^-$ signal peaked at higher pressure than the...
SO⁻ signal and rose more gradually. Even though direct S⁻ / N exchange (to produce SO$_2^-$) would appear exothermic, there is likely a large barrier. Most of the production likely followed a two-step process: S⁻ + NO$_2$ → SO⁻; SO⁻ + NO$_2$ → SO$_2^-$.

This is consistent with the SO$_2^-$ peak appearing just below 1 mTorr where 2 collisions may be expected on average according to the hard sphere calculations in section 9.2. Electron transfer to NO$_2$ was likely the dominant SO⁻ and SO$_2^-$ reaction product loss channel as indicated by their attenuation slopes and SO⁻ + NO$_2$ measurements. Hughes et al. (1973) have also measured a moderate reaction rate $k = 4.3 \times 10^{-10}$ cm$^3$molecule$^{-1}$s$^{-1}$ at 0.3 eV lab frame kinetic energy for the SO$_2^-$ electron transfer. Higher pressure trends for SO⁻ will be discussed below.

Production of NS⁻ peaked at approximately $10^{-5}$ the initial S⁻ current. This reaction should be endothermic and there is likely a barrier associated with N capture. However, for $K_0 = |q|\Delta V_{ISAS} = 6.3$ eV there would initially be $K_R = 3.7$ eV available for conversion in the centre of mass, exceeding the estimated reaction energy threshold by 3 eV. Furthermore, the kinetic energy distribution of the injected S⁻ ions was not measured and > 1% may have been > 10 eV higher in kinetic energy than that associated with $|q|\Delta V_{ISAS}$ (see section 10.3.6). With $\text{EA(NS)} = 1.194$ eV (electron affinity), the subsequent losses of NS⁻ were likely dominated by electron transfer to NO$_2$.

The NSO$_2^-$ anion has been discussed in section 10.3.2. In Figure 10-10 there is an initial rise in NSO$_2^-$ production and then a plateau at $4 \times 10^{-5}$ the initial S⁻ current. Once the molecular anion is formed, given the expected large electron affinity, electron transfer to NO$_2$ should be highly endothermic. Molecular formation likely involves at least two collisions as the S atom should form the centre of a triangular molecule with N and O at the vertices. Upon formation of an S⁻•NO$_2$ compound in an excited state, there would then be competition from the electron transfer and atom capture reaction channels and from direct dissociation so that NSO$_2^-$ formation may have represented a highly improbable reaction under the experimental conditions. Under these experimental conditions, the appearance cross section appears to be tiny, $6.2 \times 10^{-20}$ cm$^2$.

The structure of the NSO$_2^-$ anion was not determined, only its atomic components from the stripping fragments and ionization detector spectra. However, at higher pressures it is not unreasonable to expect enough collisions to have taken place for molecular formation and energy dissipation. Furthermore, the bond was strong enough to survive the tandem accelerator acceleration gradient of about 6.3 kV/cm. Weakly bound species are known to be dissociated in such gradients, for example Dy⁻ (Nadeau et al. 1994).
When injecting SO\(^-\), the initial rates of S\(^-\) and SO\(_2\)\(^-\) production were very similar. This is especially surprising considering that SO\(_2\)\(^-\) production should be exothermic and S\(^-\) endothermic (Table 10.7). A cross section was not calculated because the curves did not show good linearity on either linear or log\(_{10}\) plots (see discussion in section 10.5). Using \(K_0 = |q|\Delta V_{ISAS} = 6.3\) eV, initially there is at least \(K_R = 3.2\) eV available for conversion during the reaction, 1 eV above the estimated threshold for SO\(^-\) + NO\(_2\) \rightarrow S\(^-\) + NO\(_3\). Furthermore, as discussed for SO\(^-\) + O\(_2\) and in section 10.3.6, the ion beam kinetic energy distribution and distribution of SO\(^-\) excited states was not known. Consistent with other sources, > 1% of the ion beam could be > 10 eV above 6.3 eV whereas the observed peak level of S\(^-\) represents < 1% of the initial SO\(^-\) current.

Once created, both S\(^-\) and SO\(_2\)\(^-\) reaction products showed large attenuations. Besides the decreasing amount of reactant, S\(^-\) can interact with NO\(_2\) for SO\(^-\) production but will mostly be lost by electron transfer to NO\(_2\). Likewise, SO\(_2\)\(^-\) is likely mostly lost through electron transfer with NO\(_2\) given their electron affinities, and Hughes et al. (1973) have measured a reaction rate of \(4.3 \times 10^{-10}\) cm\(^3\)molecule\(^{-1}\)s\(^{-1}\) at 0.3 eV lab frame kinetic energy for the electron transfer.

On the other hand, both S\(^-\) and SO\(^-\) attenuations showed onset of a plateau near 6 mTorr at 7 orders of magnitude compared to the base pressure currents. The S\(^-\) and SO\(^-\) products from reactions in the cell also showed attenuation plateaus beginning at 6 mTorr and at similar levels compared to the injected beam’s initial current. The bottom left panel of Figure 10-10 was included in order to compare the trends for S\(^-\) and SO\(^-\) as reactants and reaction products.

In particular, although the plateau levels of S\(^-\) and SO\(^-\) for both reaction products and reactants were the same relative to the initial injected ion beam current, relative attenuations were different. The injected S\(^-\) and SO\(^-\) were attenuated by 7 orders of magnitude. On the other hand, the reaction products S\(^-\) and SO\(^-\) showed only 4 orders of attenuation relative to their peak abundances before onset of the plateaus. Other reaction products did not show such similarity.

By 6 mTorr in the current system with the \(\Delta V_{ISAS}\) used, the anions (reactants and reaction products) were likely approaching thermal kinetic energy. The observed trends for S\(^-\) and SO\(^-\) are suggestive of an equilibrium having been reached. The relative abundances may have arisen from the branching of reaction channels after adduct formation. For example, there may be a process such as S\(^-\) + NO\(_2\) \rightarrow S\(^*\)NO\(_2\) \rightarrow NO\(_2\)\(^-\), SO\(^-\), S\(^-\), NSO\(_2\)\(^-\), NS\(^-\). In this model, S\(^*\)NO\(_2\) \rightarrow SO\(^-\) or S\(^-\) would have similar branching ratios at equilibrium. When injecting SO\(^-\), the plateau may in fact be a symptom of the S\(^-\) produced during initial collisions.
Regardless of the exact mechanisms, the data show that the SO\(^-\) reaction product signal is about half that of the S\(^-\) signal at the S\(^-\) + NO\(_2\) plateau. Likewise at the SO\(^-\) + NO\(_2\) plateau, the S\(^-\) reaction product signal is about half that of the SO\(^-\) signal. This would suggest that at least ¼ of the S\(^-\) + NO\(_2\) plateau is due to anion–NO\(_2\) interactions within the collision cell.

Combined with the results of section 10.3.5.1, half of the S\(^-\) + NO\(_2\) plateau has been plausibly described. Given the very low level, the other half of the plateau may represent the branch for S\(^-\)•NO\(_2\) → S\(^-\) dissociation. At this point such an assertion is more of a conjecture and other explanations, such as excited states, must also be considered. However, it does point to a possible advantage to maintaining higher anion kinetic energy for isobar separation when the analyte would not be destroyed. For example, electron transfer can be rather long range. There may be an advantage to using lower gas pressures over a longer interaction region or in an ion trap to avoid complex or adduct formations (that may lead to unwanted interference feedback channels) while adequately facilitating the desired electron transfer.

10.3.6  A Note on Sputtered Anion Beam Energy Distributions

Sputtering is a relatively violent and complicated process (thoroughly reviewed in Betz and Wien 1994), and typical AMS Cs\(^+\) sputter sources are known to produce relatively large kinetic energy spreads in the case of atomic anions. The kinetic energy distributions of emitted atomic anions are strongly influenced by the target matrix, charge exchange processes when leaving the target surface, and any molecular break-up processes that produce the anion. Molecular anion beam energy spreads are further complicated by formation processes that are believed to generally take place at or near the target surface and typically have a much smaller ‘high energy tail’ than atomic anion beams, but may also form from dissociative processes (eg. electron loss from a dianion or cluster break-up).

In the case of atomic anions, the high energy tail can extend to tens of eV above the peak kinetic energy at the level of 1% peak intensity. For example, Liu et al. (2002) show F\(^-\) and O\(^-\) energy distributions from generation in an rf plasma anion source with extraction to 20 keV and deceleration to 40 eV in a cooler (see section 6.3.1). The un-cooled anion beam high energy tails extend more than 13 eV above the peaks at levels > 1% peak intensity.

Doucas (1977) studied anion beam kinetic energy spreads from a Middleton-type Cs sputter source using 20 keV Cs\(^+\). Beams of C\(^-\), S\(^-\) and I\(^-\) sputtered from graphite, PbS and NaI respectively and accelerated to 20 keV had typical full width half maximum (FWHM) kinetic
energy distributions of 13.1, 10.9 and 9.7 eV respectively. The C−, S− and I− high energy tails extended 30, 20 and > 50 eV above the kinetic energy at the peak of the distribution respectively at levels on the order of 1% peak intensity. More examples may be found in Jurela (1975).

Larger molecules produced from sputtering are generally observed to have smaller kinetic energy distributions. However, the high kinetic energy tails of smaller molecular anions can still be quite significant. For example, Gnaser (2000) shows energy distributions of Si_{x}C_{y}^{−} (x = 1, 2; y an integer ≥ 1) sputtered from SiC at 14.5 keV Cs^{+} kinetic energy. In Figure 1, at 10^{-2} peak intensity the SiC^{−} ion beam high energy spread is > 20 eV above the peak kinetic energy, and SiC_{2}^{−} is > 15 eV above the peak kinetic energy at 10^{-2} peak intensity. Likewise in Figure 2, both the Si_{2}C^{−} and Si_{2}C_{2}^{−} high energy tails are > 10 eV above the peak kinetic energy at a level of 10^{-2} peak intensity. This is consistent with the proposed energy distribution used to explain the observed SO^{−} + O_{2} → S^{−} reaction (section 10.3.4, see chapter 7 for ion source details).

Sputtering with Cs^{+} at 14 or 20 keV versus 4 keV may result in slightly elevated high and low energy tails as more atoms would be ejected from the target at higher kinetic energy and there may be larger populations of excited states. However, anion formation depends on many factors such as those noted above and the speed with which atoms escape from the target surface and the surface work function (discussed in Jurela 1973). Over the sputtering energy ranges considered and for anion beam energy spread populations below 200 eV, the relative populations should be on the same order of magnitude.

A fairly large kinetic energy spread, ΔK_{0}, could have been injected into the ISA with the ISA test bed magnet and φ2 mm aperture arrangement used (Figure 7-1). For ion beams initially accelerated to K_{0} = 20 keV, ΔK_{0} = 180 eV could have been injected into the ISA assuming the ion beam ‘object’ image were well defined (see Table 2.1). The system did not incorporate an electric analyzer and, typically, the slits at FC1 were set ‘wide open’ (typical settings, section 7.6) so that the actual ΔK_{0} may have been even greater.

Ion beam kinetic energy spreads could be verified by any number of means. One could directly measure the energy spread after deceleration in the ISA. Such an attempt was made but results were obscured by fringing field effects. On the other hand, different Cs^{+} sputtering energy or different target materials could be used. For example, the SO^{−} energy spread depends on both the physical ejection of molecules and atoms, and the ion source reactions that led to the molecular anion formation.
When available, there will also be a spread in the ground to excited states of anions emanating from the sputter region that will affect reactivity and the reaction channels available. Excited states have not been discussed but are surely present, and may play a relatively important role in the reactions and attenuation plateaus observed. For gas-phase reaction studies with a system like the ISA and ISA test bed, the importance of moderating the ion beam energy spread and de-excitation of excited states by incorporating a cooling cell before the reaction cell should not be understated.

10.4 $^{12}\text{C}_3^-$ + Ar and NO$_2$

Like sulphur, carbon is ubiquitous in Earth’s environment and in much of the observed solid universe. The $^{12}\text{C}_3^-$ molecular anion is an isobar of $^{36}\text{Cl}^-$ and is readily produced in sputter ion sources. Initial S$^-\rightarrow$Cl$^-$ attenuation tests were performed using $q = +3$ after stripping with $V_T = 1.75$ MV. Under these conditions lower mass, smaller molecular anions have been found to be efficiently dissociated in tandem accelerators and the Cl stripping yield was expected to be about 30% (based on Wittkower and Betz 1973). However, for $m = 36$ amu measurements, $36/3 = 12/1$ and the fragments $^{12}\text{C}_3^-\rightarrow^{12}\text{C}^+$ had the same magnetic and electric rigidity as the $^{36}\text{Cl}^{+3}$ ions.

Ideally a stripping charge state is chosen so that $m/q$ is not an integral number in order to avoid interferences from the fragments of molecular anions that may dissociate during stripping. Mass 36 amu is particularly fussy as it is divisible by 1, 2, 3, 4 and 6. High efficiency equilibrium stripping to bigger charge states requires higher terminal voltages than to smaller charge states. In the case of Cl in Ar, stripping yields to $q = +5$ are given in Wittkower and Betz (1973) as 0.590% at 1 MV, 3.03% at 2 MV and 18.4% at 4 MV.

On the other hand, a major goal of this project was to increase the analytical capabilities of smaller AMS systems. Currently, ≤ 1 MV AMS systems use higher stripper pressure and lower charge states for detection. At higher stripping pressure there may even be an advantage to using the $q = +1$ charge state for smaller atomic anions as the fragments from smaller molecular anions, such as $^{18}\text{O}_2^-$ and $^{12}\text{C}_3^-$ for $^{36}\text{Cl}^-$ measurements, would not add to the background. Molecular destruction is not 100% efficient and any $^{12}\text{C}_3^+$ or $^{18}\text{O}_2^+$ would still add to the background. To that end, attenuation of $^{12}\text{C}_3^-$ was studied briefly. Because of the relatively weak electron affinity of O$_2$ (0.45 eV), it is expected that O$_2^-$ would have a large attenuation cross section in NO$_2$ through electron transfer.
Figure 10-11: $^{12}\text{C}_3^-$ + Ar and NO$_2$ Attenuations and Ionization Detector Spectra for $^{12}\text{C}^+$

**Attenuations vs. Pressure**

Top left panel: $^{12}\text{C}_3^-$ was generated from a graphite target and analyzed using the full AMS system for $^{12}\text{C}_3^-$ detection using typical ion source and AMS settings (section 7.6, $V_T = 1.75$ MV). From FC2 currents, the ratio $^{36}\text{S}/^{32}\text{S} < 5 \times 10^{-7}$ so that measurements did not have a significant $^{36}\text{S}$ background. The ionization detector channel spectra (right column) also indicate that the beam was mainly $^{12}\text{C}_3^-$. The collision cell with $\phi 2$ mm apertures (L2 – L5) and without gradient bars was used (Figure 7-4) with $\Delta V_{\text{ISAS}} = 8.0$ V (Eq 7.1).

Bottom left panel: Comparison between the $^{12}\text{C}_3^-$ + NO$_2$ attenuation and $^{32}\text{S}^-$ + NO$_2$ curves B and F in Figure 10-8. Data was taken with different targets and normalized to the respective measurement base pressure transmissions. In particular, the $\Delta V_{\text{ISAS}} = 8.0$ V and 12 V curves were taken with the collision cell with $\phi 2$ mm apertures (L2 – L5) and without gradient bars, while the $\Delta V = 5.3$ V curve was taken using the cell with gradient bars and $\phi 3$ mm apertures (Figure 7-4).

Right bottom panel: Ionization detector channel spectra showing the $^{12}\text{C}^+$ and the 2 and 3 coincident $^{12}\text{C}^+$ peaks from $^{12}\text{C}_3^- \rightarrow ^{12}\text{C}^+$ (see section 10.3.2) at 4 pressures. Counts were accumulated for 100 s at each pressure.

Right top panel: Attenuation of each peak in the $^{12}\text{C}_3^- \rightarrow ^{12}\text{C}^+$ ionization detector peak spectrum (see bottom right panel) versus NO$_2$ pressure and normalized to the base pressure $^{12}\text{C}_3^- \rightarrow ^{12}\text{C}^+$ signal.
The top left panel of Figure 10-11 shows $^{12}\text{C}_3^-$ attenuation in Ar and NO$_2$ with $\Delta V_{\text{ISAS}} = 8$ V. A graphite target was used to reduce $^{36}\text{S}^-$ interference, using typical settings for the ion source and AMS (section 7.6, ion source $V_s = -20.7030$ kV) for $^{12}\text{C}_3^- \rightarrow ^{12}\text{C}^+$ detection. The collision cell did not have gradient bars and had $\phi 2$ mm apertures at the entrance and exit (L2 – L5, Figure 7-4). Currents at FC2 were: $^{12}\text{C}^- = 300$ nA, $^{12}\text{C}_2^- = 135$ nA, $m = 32$ amu ($^{32}\text{S}^-$) = 0.03 nA, and $^{12}\text{C}_3^- = 13$ nA. Assuming $^{36}\text{S}/^{32}\text{S} = 0.02\%$ (Baum et al. 2002), the ratio $^{36}\text{S}^-/^{12}\text{C}_3^- < 5 \times 10^{-7}$ so that measurements did not have a significant $^{36}\text{S}^-$ background. The base pressure (Pisa = $2 \times 10^{-7}$ Torr) $^{12}\text{C}_3^- \rightarrow ^{12}\text{C}^+$ signal at FC7 was 1.2 nA for a transmission FC2 to FC7 of 9%.

The bottom right panel of Figure 10-11 shows the ionization detector channel spectra for 8, 9, 10 and 13 mTorr NO$_2$ cell pressure. An accumulation time of 100 s was used for each spectrum. There are three, well resolved peaks that appear as would be expected for a $^{12}\text{C}_3^- \rightarrow ^{12}\text{C}^+$ spectrum (discussed in section 10.3.2, particularly bullet 2): the single $^{12}\text{C}^+$ peak is 2.5 times larger than the peak corresponding to 2 coincident $^{12}\text{C}^+$ ions, which in turn is 5 times larger than the triple add-up peak. It is the triple add-up peak that would interfere with a $^{36}\text{Cl}^- \rightarrow ^{36}\text{Cl}^{+3}$ signal. The top right panel shows the intensity of each peak normalized to the base pressure $^{12}\text{C}_3^- \rightarrow ^{12}\text{C}^+$ FC7 signal versus NO$_2$ pressure over the range 8 – 13 mTorr. All 3 peaks showed similar attenuations with pressure. This lends further re-assurance that the signal was indeed revealing $^{12}\text{C}_3^-$ behaviour and was not obscured by isobaric interferences such as $^{36}\text{S}^{+3}$.

Since $^{12}\text{C}_3^-$ attenuation data were not taken with the second reaction cell with gradient bars and larger apertures, the left bottom panel was included in Figure 10-11 for comparison between the different collision cells and between C$_3^-$ and S$^-$ attenuations in NO$_2$. From the S$^-$ data, while the overall transmission through the collision cell was improved by the addition of gradient bars and widening of the apertures, the overall attenuation was consistent with the two cells. This may be a reflection the large S$^- +$ NO$_2$ attenuation cross section. The observed C$_3^- +$ NO$_2$ attenuation cross section was similarly large, 4.2 x $10^{-15}$ cm$^2$ (section 10.5). While it was 2/3 the value observed for S$^-$ under the same conditions, the overall attenuation of C$_3^-$ was about 3 times greater than that of S$^-$ by the respective attenuation plateaus.

Reaction channels were not investigated for $^{12}\text{C}_3^- +$ NO$_2$, however some comments may be made. First, the electron affinity $\text{EA}(C_3) = 1.981$ eV (Haynes and Lide 2011) is 0.3 eV less than $\text{EA(NO}_2$) and a large attenuation by electron transfer may be expected in NO$_2$ gas.

Notwithstanding, a bond dissociation energy for C–C$_2$ can be estimated as $D(C–C_2) = 7.60$ eV from heats of formation as compiled by Chase (1998: $\Delta_f^0(C_3) = 820.06$ kJ/mol (8.49
10—194

\[ \Delta H^0 (C_2) = 837.74 \text{ kJ/mol (8.67 eV)}, \quad \Delta H^0 (C) = 716.67 \text{ kJ/mol (7.42 eV)} \]. Neglecting barriers, \[ \Delta H (C_3^- + NO_2 \to C_2^- + CO + NO) = -1.67 \text{ eV} \] looks to be exothermic. Furthermore, with initial kinetic energy \( K_0 \geq |q|\Delta V_{ISAS} = 8.0 \text{ eV}, \quad K_R \geq 4.5 \text{ eV} \) (Eq 6.35) was the energy available for conversion during initial collisions.

Other oxides, such as C_3O that has an electron affinity > 1 eV, may also have been formed. Although these may not have been the dominant reaction channels, the onset of an attenuation plateau for \( ^{12}C_3^- + NO_2 \) between 8 and 10 mTorr cell pressure may have to do with a reaction feedback cycle, a weakly bound adduct or cluster formations as posited as a partial source for the \( S^- + NO_2 \) plateau.

In Ar, \( ^{12}C_3^- \) had been attenuated by 90% by 6 mTorr. The initial kinetic energy was \( K_0 \geq |q|\Delta V_{ISAS} = 8.0 \text{ eV} \) so that \( K_R \geq 4.2 \text{ eV} \) was the energy available for conversion during initial collisions. For \( K_R \geq D(C^-C_2) \) for \( ^{12}C_3^- \) on Ar, initially \( K_0 \geq 14.4 \text{ eV} \) would have been needed, more than 6 eV above \( |q|\Delta V_{ISAS} \). Such an energy spread should not account for more than a few percent of the ion beam at most (section 10.3.6). Multiple collisions, however, could have excited vibrational states resulting in CID, and there may have been some effect due to the need to use 30 V – 40 V on the inner cell apertures to maintain high transmission.

On the other hand, the overall attenuation was consistent with other atomic anions as plotted in Figure 9-5. With \( K_R \geq 4.2 \text{ eV} > 2\times EA(C_3) \), electron detachment could have proceeded. Furthermore, \( ^{12}C_3^- \) is less massive than Ar (on average) so that scattering at all angles was possible and electron detachment and scattering likely accounted for a significant portion of the observed losses.

Nonetheless, the overall attenuation of \( ^{12}C_3^- \) was greater than that of \( S^- \) in NO_2, albeit at a higher cell pressure, while the attenuation cross section was smaller.

10.5 Reaction and Total Attenuation Cross Section Estimates

Zeroth order appearance or attenuation rates are constant on a linear plot with respect to the interaction variable. For the measurements in this chapter, appearance or attenuation was measured against collision cell gas pressure, which affects the average number of collisions that an ion will have. Let the initial amount (eg signal at FC7) of reactant be \( X_0^- \). The normalized slope of a linear plot of product \( Y^- \) versus pressure \( P \) is,
Eq 10.1

\[ L_0 = \frac{\Delta \left( \frac{Y^-}{X_0} \right)}{\Delta P} \]

Then, the zeroth order cross section, \( \sigma_0 \), between \( X^- + \text{gas} \rightarrow Y^- \) can be determined by:

Eq 10.2

\[ \sigma_0 = |L_0| \cdot \frac{k_B T}{l} \]

where \( k_B \) is Boltzmann’s constant, \( T \) is the gas temperature and \( l \) is the path length of interaction. For \( X^- \) attenuation measurements, \([Y^-] = [X^-]\) and all else is the same.

First order reaction appearance or attenuation rates plot linearly on a log plot versus the changing interaction variable (pressure for this chapter). For attenuation measurements, the relationship between pressure and reactant should be analogous to the radioactive decay equation (see B2 of Appendix B). For appearance measurements, the exponent of equation B2 becomes positive and ‘\( N_0 \)’ (see equation) is not used. The 1st order reaction slope has the form:

Eq 10.3

\[ L_1 = \frac{\log \left( \frac{Y^-}{X_0} \right)}{\Delta P} \]

If \( \log = \log_e = \ln \) (\( \log_e \) is the natural logarithm also written as \( \ln \)) is used, the reaction cross section can then be calculated from:

Eq 10.4

\[ \sigma_1 = |L_1| \cdot \frac{k_B T}{l} \]

Otherwise \( \sigma_1 \) must be multiplied by the conversion factor \( \ln(a) \) where the original slope was calculated from a \( \log_a \) representation. For example, if the slope were calculated from a \( \log_{10} \) plot then Eq 10.4 would need to be multiplied by \( \ln(10) \). Otherwise, \( \sigma \) has the same form in equations 10.2 and 10.4.

Measurements were conducted at room temperature and a value of \( T = 298 \) K was used for cross section calculations.

No attempt has been made to calculate an average ion path length or trajectory amplitude. Ion beam energy spreads were not moderated by an electric analyzer or cooling cell and, coupled with the divergence introduced during deceleration in the ISA, there was likely a large variation in energies and amplitudes. Sputter produced ion beam energy spreads have been discussed in section 10.3.6 and ion trajectory dependence on kinetic energy in chapter 5. Motion is further complicated by collisions within the cell.
However, when the rf quadrupole trajectory period of an ion, $T_0(\omega)$ (Eq 5.13 for low $q_2$), is on the order of the number of cycles that an ion spends within the quadrupole instrument, $L_{nr}$ (Eq 4.28), then the path length of the ion approaches the physical length of the quadrupole instrument. The correspondence is better for lower-amplitude trajectories and $q_2 < 0.2$ (see chapter 5, for example Figure 5-1 and Figure 5-8). Most experimental conditions had $q_2 < 0.15$. A path length $l = 15$ cm, the length of the collision cell, was assumed for cross section calculations. These represent an upper limit and provide a useful guide for understanding the nature of the underlying processes observed during experiments.

A lower limit for the initial kinetic energy of ions injected into the cell is $K_0 = |q|\Delta V_{ISAS}$ where $|q|$ is the magnitude of the ion charge and $\Delta V_{ISAS}$ is the ion source – ISA deck voltage offset given by Eq 7.1. As discussed in section 10.3.6, this will underestimate $K_0$ for many of the ions, especially since the test bed did not include an electric analyzer nor was there a cooling cell before the reaction cell. It also neglects any initial radial kinetic energy ($K_r$) and rf heating. From section 8.1.2, at base pressure $K_r < 0.5$ eV appeared to apply to only about 1% of the Cl$^-$ ion beam. Nonetheless, $K_0$ and the mass of the incident ion can be used to determine an ion speed, $v$, (eg Table A 5) that can be used with the cross section to calculate a reaction rate coefficient, $k$, according to Eq 6.31. These estimates give the general order of the reaction rate coefficient and are useful for comparing the reactions observed with the ISA to those in the literature.

Cross sections were calculated only when curves showed linearity over a span of at least 4 points on either a linear or log$_{10}$ plot. As an example of the ambiguities that may arise otherwise, consider SO$^- + NO_2 \rightarrow S^- and SO_2^-$ curves in Figure 10-10. Both had similar appearance slopes while the SO$_2^-$ channel was calculated to be exothermic while the S$^-$ endothermic. If the first two points ($0 - 0.25$ mTorr) were used assuming a 1$^{st}$ order reaction then cross sections for SO$^- + NO_2 \rightarrow S^-$; SO$_2^-$ would be very large, 4.1 $\times$ 10$^{-14}$ cm$^2$ and 4.2 $\times$ 10$^{-14}$ cm$^2$ respectively, with a very large reaction rate coefficient, 1.9 $\times$ 10$^{-8}$ cm$^3$molecule$^{-1}$s$^{-1}$ (same for both). If the first 3 points ($0 - 0.5$ mTorr) were used assuming a zeroth order reaction then the associated cross sections would be 1.7 $\times$ 10$^{-17}$ cm$^2$ and 6.1 $\times$ 10$^{-18}$ cm$^2$ with associated reaction rate coefficients of 8.0 $\times$ 10$^{-12}$ and 2.8 $\times$ 10$^{-12}$ cm$^3$molecule$^{-1}$s$^{-1}$ respectively. More information is needed over 0 – 0.5 mTorr in order to determine the actual nature of these reactions.

Quite on the contrary, there is a relative litany of data for S$^- + NO_2$ attenuation in the ISA. It spans $4.5$ V $\leq \Delta V_{ISAS} \leq 8$ V, all of the curves showed good agreement and there is good linearity in the range 0 – 2.5 mTorr pressure (Figure 10-8). A linear regression was applied to all
data points in the plot (from all 6 curves, as if they were 1 data set) from 1 – 2.5 mTorr. The slope was used to find the average cross section measured over this range of $\Delta V_{\text{ISAS}}$ for $S^- + \text{NO}_2$ attenuation, $6.6 \times 10^{-15} \text{ cm}^2$ (Table 10.8), and differed from individual cross sections by < 2%.

Table 10.8 on the last page of this chapter presents the calculated cross sections from this chapter.

10.6 Summary and Conclusions

With the current ISA design and test bed, among the gases surveyed with $4.5 \text{ V} \leq \Delta V_{\text{ISAS}} \leq 12 \text{ V}$, NO$_2$ has been found to yield the largest $S^-$ attenuation with cross section $6.6 \times 10^{-15} \text{ cm}^2$. However, there is an attenuation plateau at $10^{-7}$ of the original $S^-$ signal with onset near 6 mTorr pressure. Similarly, a cross section of $4.2 \times 10^{-15} \text{ cm}^2$ has been observed for $C_3^- \text{ attenuation in NO}_2$, but there is onset of a plateau at 8 mTorr cell pressure at $10^{-8}$ the initial beam intensity. Nonetheless, at 6 mTorr NO$_2$ pressure a Cl$^-$ attenuation on the order of $60 - 70\%$ can be expected vs $S^-$ and $C_3^-$ attenuations on the order of $3 \times 10^{-7}$ for a relative attenuation of $2 \times 10^{-6}$, at least for the range of $\Delta V_{\text{ISAS}}$ used ($4.5 \text{ V} - 8 \text{ V}$).

Furthermore, $^{36}\text{S}$ is the major isobar of $^{36}\text{Cl}$ but represents 0.02% S in many natural samples. Also, the sputter ratio $^{12}\text{C}_3^-/^{12}\text{C}^-$ was found to be 4% and the interfering $3\text{C}^+$ add-up peak from $^{12}\text{C}_3^-$ stripping to $^{12}\text{C}^+$ ($V_T = 1.75 \text{ MV}$) for $^{36}\text{C}^+$ was 1% the C$^+$ peak. With some sample preparation to reduce impurities to parts per million, this leads to a possible attenuation of interferences $^{36}\text{S}^-/\text{Cl}^- \sim 4 \times 10^{-6}$ and $^{12}\text{C}_3^-/\text{Cl}^- \sim 1.2 \times 10^{-16}$ at 8 mTorr NO$_2$ pressure, suggesting that the ISA with NO$_2$ can be an effective isobar filter for $^{36}\text{Cl}^-$ analyses by AMS.

Two likely sources of the $S^-$ plateau have been identified.

- The first is from phenomena unrelated to reactions within the collision cell. Some high kinetic energy $S^-$ ions will be neutralized before the deceleration stage of the ISA, some of which will pass the ISA apertures and be re-ionized after passing through the reacceleration region. There may also be some contribution from the high energy tail of the $S^-$ ion beam. Both of these effects can be reduced with better differential pumping and addition of an electric analyzer to the test bed and a cooling cell before the ISA. A slight offset of the ion trajectory so that there is not a straight line of sight through the magnet focus, ISA and tandem accelerator stripping canal would also reduce background.
- The second has to do with reactions within the collision cell such as formation of adducts, clusters or compounds in excited states that have branching ratios to $S^-$. Use of a segmented
A quadrupole may actually lower the observed large attenuation reaction plateaus by maintaining ion energies above the threshold for such formations. Additionally, an rf frequency resonant with a known major compound that ‘reproduces’ $S^-$ could be added for compound ejection before $S^-$ ‘reproduction’, as in a ‘notch’ filter.

All major attenuation curves studied have been found to plateau, not at the same level or pressure in all cases but consistent for a given anion. While not all roots for the plateaus have been investigated, for example un-reactive excited states, several sources likely contribute to each plateau concurrently.

Conversely, transmission through CH$_4$ > 60% (> 90% for Cl$^-$), has been observed (section 9.3). For CH$_4$ pressures > 6 mTorr ions were predicted by a hard sphere ‘free drift’ model (section 9.2) to be approaching thermal kinetic energy on average, suggesting that CH$_4$ could be a very effective cooling gas. There are several advantages to using CH$_4$ instead of He or Ar (as commonly used) for cooling lower mass anions, especially when they are less massive than Ar, including:

- The CH$_4$ hard sphere cross section is comparable to Ar and much greater than He
- The CH$_4$ Langevin cross section $>>$ Ar and He
- The hard sphere maximum energy loss in CH$_4$ is comparable to Ar ($\sim$ 80%, Figure 6-3) and is much greater than that for He. At the same time, the energy available for conversion during a collision with CH$_4$, $K_R$(CH$_4$) $<<$ $K_R$(Ar). The number of collisions required for cooling in CH$_4$ should be comparable to that of Ar, but much less than He (eg Figure 9-3, Figure 9-4)
- The maximum scattering angle on CH$_4$ is much less for Al, Si, S, Cl than in Ar (no back-scattering in CH$_4$)
- CH$_4$ pumping is less demanding than He and CH$_4$ is more cost effective currently

However, reactive losses and background from impurities may be larger with CH$_4$ than He or Ar as the latter are noble gasses that it may not be the best gas for all anion studies.

This chapter also introduced a new technique for measurements in physical chemistry that may be called rf quadrupole accelerator mass spectrometry for the study of gas-phase anion reactions (RFQ–AMS–GPAR). Advantages include relatively unambiguous identification of the atomic constituents of molecules, an ion source that readily produces a wide variety of anions.
with large current, and a very large dynamic range (> 16 orders of magnitude), and high 
sensitivity (on the order of counts per day).

Molecular anion identification through detection of atomic cation fragments after 
stripping in the accelerator terminal was described, and was demonstrated with spectra from 
NSO$_2$\textsuperscript{−} and C$_3$\textsuperscript{−}. The S-atom containing reaction product \textsuperscript{VT scans} shown in Figure 10-4 also 
showed clear differences in the relative strengths of reaction channels for S\textsuperscript{−} in N$_2$O, NO$_2$ and O$_2$. 
Although the ion energies were not well moderated, reaction cross sections for S\textsuperscript{−} in NO$_2$ and O$_2$ 
in the range $10^{-14}$ to $10^{-20}$ cm$^2$ were observed.

Lack of moderation of the ion beam energy spread led to many ambiguities. These can be 
mitigated by the introduction of an electric analyzer to the test bed and a cooling cell to the ISA, 
and possibly by eliminating the straight line of sight between the test bed injector magnet, ISA 
and accelerator stripping canal.
Table 10.8: Cross Section and Reaction Rate Coefficient Estimates for C$_3$-, S-, SO$_2$-, NO$_2$- + NO$_2$, O$_2$

| Reaction | Order$^a$ | Initial Ion Kinetic Energy Estimate [eV]$^b$ | Pressure Range$^c$ [mTorr] | Number of Points$^c$ | Figure$^c$ | Cross Section $[\times 10^{-15} \text{ cm}^2]^b$ | Rate Coefficient $[\times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}]^b$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>S$^-$ + NO$_2$ $\rightarrow$ NSO$_2^-$$^d$</td>
<td>0</td>
<td>5.8</td>
<td>0 – 1.5</td>
<td>7</td>
<td>10–10</td>
<td>0.000062</td>
<td>0.000037</td>
</tr>
<tr>
<td>S$^-$ + O$_2$ $\rightarrow$ SO$^-$$^d$</td>
<td>0</td>
<td>4.8</td>
<td>0 – 0.5</td>
<td>5</td>
<td>10–7</td>
<td>0.045</td>
<td>0.024</td>
</tr>
<tr>
<td>S$^-$ + NO$_2$ $\rightarrow$ NO$_2^-$$^d$</td>
<td>0</td>
<td>5.8</td>
<td>0 – 1</td>
<td>4</td>
<td>10–10</td>
<td>1.0</td>
<td>0.59</td>
</tr>
<tr>
<td>SO$^-$ + O$_2$ $\rightarrow$ S$^-$</td>
<td>0</td>
<td>4.8</td>
<td>0 – 0.5</td>
<td>4</td>
<td>10–7</td>
<td>0.028</td>
<td>0.012</td>
</tr>
<tr>
<td>SO$^-$ + NO$_2$ $\rightarrow$ NO$_2^-$$^d$</td>
<td>0</td>
<td>5.2</td>
<td>0 – 1</td>
<td>4</td>
<td>10–10</td>
<td>1.2</td>
<td>0.55</td>
</tr>
<tr>
<td>SO$^-$ + O$_2$ $\rightarrow$ SO$_2^-$$^d$</td>
<td>1</td>
<td>4.8</td>
<td>0 – 0.5</td>
<td>4</td>
<td>10–7</td>
<td>18</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Overall Attenuation Cross Sections and Rate Coefficients

| Reaction | Order$^a$ | Initial Ion Kinetic Energy Estimate [eV]$^b$ | Pressure Range$^c$ [mTorr] | Number of Points$^c$ | Figure$^c$ | Cross Section $[\times 10^{-15} \text{ cm}^2]^b$ | Rate Coefficient $[\times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}]^b$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$- + NO$_2$</td>
<td>1</td>
<td>8</td>
<td>0 – 8</td>
<td>6</td>
<td>10–11</td>
<td>4.2</td>
<td>2.7</td>
</tr>
<tr>
<td>S$^-$ + NO$_2$</td>
<td>1</td>
<td>6.1$^d$</td>
<td>0 – 2.5</td>
<td>40$^d$</td>
<td>10–8</td>
<td>6.6$^d$</td>
<td>4.0$^d$</td>
</tr>
<tr>
<td>SO$^-$ + NO$_2$</td>
<td>1</td>
<td>5.3</td>
<td>0 – 1.5</td>
<td>8</td>
<td>10–10</td>
<td>7.1</td>
<td>3.3</td>
</tr>
<tr>
<td>S$^-$ + O$_2$</td>
<td>1</td>
<td>4.8</td>
<td>2 – 7</td>
<td>7</td>
<td>10–7</td>
<td>0.66</td>
<td>0.36</td>
</tr>
<tr>
<td>SO$^-$ + O$_2$</td>
<td>1</td>
<td>4.8</td>
<td>0.5 – 5</td>
<td>4</td>
<td>10–7</td>
<td>1.1</td>
<td>0.50</td>
</tr>
</tbody>
</table>

---

$^a$ Cross sections were calculated using Eq 10.1 and 10.2 because the data plotted linearly on a linear plot for order 0 and were calculated using Eq 10.3 and 10.4 because data plotted linearly on a log$10$ plot for order 1. Data was included over the full range of linearity observed.

$^b$ A lower limit estimate for the ion kinetic energy based on $K_0 = |q|\Delta \text{VISAS}$ where $q$ is the ion charge and $\Delta \text{VISAS}$ is given by Eq 7.1 was used in the calculation of the rate coefficient (see text for more details).

$^c$ These columns give the pressure range, number of points and figure used in the cross section slope calculation.

$^d$ Points from all six curves in the figure within the pressure range were used to produce a linear fit and calculate a slope for the cross section. $K_0 = 6.1$ eV represents an average of the six $\Delta \text{VISAS}$ used. The line fit all inidivual data sets very well, and cross sections calculated from individual curves differed by less than 2%.
11$^{36}$Cl Reference Standards Comparison

In the summary of chapter 10 (section 10.6), a total possible attenuation of interferences from $^{36}$S$^-$ and $^{12}$C$_3^-$ was assessed for the ISA and test bed system as described in chapter 7. Based on the measured attenuations in NO$_2$ at 8 mTorr using an accelerator terminal voltage $V_T = 1.75$ MV for stripping to $q = +3$, relative attenuations of $^{36}$S$^-$/Cl$^- \sim 4 \times 10^{-16}$ and $^{12}$C$_3^-$/Cl$^- \sim 1.2 \times 10^{-16}$ were calculated. This chapter presents an initial assessment of the $^{36}$Cl analytical capabilities of the system using a set of reference $^{36}$Cl standards provided by Prof. Mark Caffee, PRIME Lab (Purdue University, Department of Physics, Indianapolis, U.S.A.) with $4 \times 10^{-13} \leq ^{36}$Cl/Cl $\leq 4 \times 10^{-11}$. Table 11.1 summarizes relevant target information. Details concerning the measurements and results are given in sections 11.1 and 11.2, and a discussion follows at the end of the chapter.

<table>
<thead>
<tr>
<th>Target ID</th>
<th>$^{36}$Cl/Cl (x $10^{-11}$)</th>
<th>Target Composition</th>
<th>Ratio Nb : AgCl (NaCl)</th>
<th>Mass Nb [mg]</th>
<th>AgCl (NaCl) [mg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z93 – 0003$^a$</td>
<td>4.16</td>
<td>AgCl + Nb</td>
<td>4.6</td>
<td>190.0</td>
<td>9.0</td>
</tr>
<tr>
<td>Z93 – 0004$^a$</td>
<td>0.442</td>
<td>AgCl + Nb</td>
<td>6.3</td>
<td>259.5</td>
<td>6.5</td>
</tr>
<tr>
<td>Z93 – 0005$^a$</td>
<td>0.120</td>
<td>AgCl + Nb</td>
<td>13.6</td>
<td>533.4</td>
<td>2.9</td>
</tr>
<tr>
<td>Z93 – 0006$^a$</td>
<td>0.0408</td>
<td>AgCl + Nb</td>
<td>8.6</td>
<td>339.4</td>
<td>4.6</td>
</tr>
</tbody>
</table>

a) PRIME Lab AMS standard reference (PRIME Lab, Purdue University, Indianapolis, U.S.A.)

A blank AgCl reference material was not included with the $^{36}$Cl reference standards. Materials were mixed with Nb and pressed into Al target holders with Cu back pins (see section 7.5) at IsoTrace Laboratory.

11.1 $^{36}$Cl/Cl = $4 \times 10^{-11}$ Measurement at $V_T = 1.75$ MV vs. NO$_2$ Pressure: A test of the $^{36}$Cl$^{+3}$ blank

This section essentially analyzes the background present in $^{36}$Cl analysis with the current test bed, ISA and AMS system (see chapter 7), using targets that had been prepared for that purpose, under a particular set of experimental conditions. An accelerator terminal voltage $V_T = 1.75$ MV was used for detection of $^{36}$Cl$^- \rightarrow ^{36}$Cl$^{+3}$ from target Z93 – 0003 versus NO$_2$ pressure in
the ISA using the collision cell without gradient bars and with φ2 mm apertures L2 – L5 (Figure 7-4). Some isobar attenuations have already been addressed in chapter 10, where it was also demonstrated that the attenuation results were the same for this collision cell and the cell with gradient bars and φ3 mm apertures L2 – L5 (eg see Figure 10-8 and Figure 10-11).

Prior to taking data, the ion source was cleaned and the base ISA chamber pressure was \( P_{\text{isa}} = 2.5 \times 10^{-7} \) Torr. Tuning for the ISA was done injecting 29 nA of \(^{37}\text{Cl}^-\) (FC2) in \( \text{NO}_2 \) and base pressure transmission FC2 to FC7 was 5.4% while transmission at 13 mTorr was 0.5%. All measurements were made using typical settings (section 7.6) with the ion source at \(-20.7\) kV, \( \Delta V_{\text{ISAS}} = 12.0 \) V (Eq 7.1) and \( V_T = 1.75 \) MV for stripping to \( q = +3 \).

11.1.1 Background

Ionization detector signal accumulation times are given in the next section but did not exceed 1000 s for any \(^{36}\text{Cl}\) measurement. The minimum signal observed was 381 c / 1000 s for \( m = 36 \) amu at channel \( q = +3 \) with 13 mTorr \( \text{NO}_2 \) in the cell, well above any observed background in this section. Less than 30 pA (at FC2) of \( m/q = 36 \) (includes signals from \(^{36}\text{Cl}^-, \quad ^{36}\text{S}^- \) and \(^{12}\text{C}_3^-\)) was injected into the ISA for \(^{36}\text{Cl}\) measurements.

First, \( \text{Ar} \) was used in the tandem accelerator stripping canal, raising the possibility of a signal from \(^{36}\text{Ar}^{+3}\). Contributions of \(^{36}\text{Ar}^{+3}\) to the blank are suppressed by the electric and magnetic analyzer requirements: \(^{36}\text{Cl}^- \rightarrow ^{36}\text{Cl}^{+3}\) leads to ions with energy \(|4e|V_T + K_0\) where \( e \) is the fundamental charge and \( K_0 \) is the kinetic energy of the anion for injection into the accelerator. Any \( \text{Ar}^{+3} \) accelerated from rest in the stripping canal would have only \(|3e|V_T\). Contributions to the blank would be from a possible high energy \(^{36}\text{Ar}^{+3}\) tail and charge changing processes with higher charge-states.

With the test bed, ISA and AMS system warmed up, and stripper \( \text{Ar} \) pressure equilibrated, the AMS system was set for \(^{36}\text{Cl}^- \rightarrow ^{36}\text{Cl}^{+3}\) detection (\( V_T = 1.75 \) MV). A vacuum gate valve between the ISA chamber and FC4 was closed to suppress contributions from the ISA and test bed. No signal was detected on the channels for \( q = +2 \) and +3 after 5000 s accumulation time, although there was a small peak on the \( q = +1 \) channel from residual \( \text{C} \) in the stripping canal deposited over years of radiocarbon analysis. Ionization of \( \text{Ar} \) in the stripping canal during anion stripping is discussed below.

Next, possible contributions from ionization of \( \text{NO}_2 \) impurities and residual gas in the ISA were tested with 12.7 mTorr \( \text{NO}_2 \) in the ISA while injecting 56 pA \(^{18}\text{O}^-\) with the afore-
mentioned gate valve open and system still set for $^{36}\text{Cl}^- \rightarrow ^{36}\text{Cl}^{+3}$ detection. In 5000 s, 3 counts had been accumulated on peak (q = +3 channel). Inserting FC4 into the ion beam path resulted in no peak signal over a 5000 s accumulation time. With FC4 out of the ion path and FC2 in the ion path (to block ion injection into the ISA), no peak signal was recorded over 1000 s.

There were no mass or energy discriminators between the ISA and accelerator so that all ions exiting the ISA, including reaction products, were potentially injected into the stripping canal. While O$^-$ was not directly injected into the accelerator, reaction products and surviving O$^-$ would have been.

On the other hand, this also means that the $^{36}\text{S}^- + \text{NO}_2$ reaction products containing $^{36}\text{S}$ are also potential sources of background for $^{36}\text{Cl}$ analyses. In particular, the $^\text{S}^- + \text{NO}_2 \rightarrow \text{NSO}_2^-\text{O}^-$ level in Figure 10-10 was more than one order of magnitude above the $^\text{S}^-$ signal at higher pressures. However, like Ar ionized in the stripping canal, $^{36}\text{S}$ from $\text{NSO}_2^-$ break-up could contribute to the $^{36}\text{Cl}$ background, but would be suppressed by the subsequent electric and magnetic analyzers because of the remaining kinetic energy after break-up.

In the end, the measurements of this section suggest that the background was well below the peaks observed during the $^{36}\text{Cl}$ measurements.

11.1.2 Results

Figure 11-1a) shows the results of the NO$_2$ pressure scan. At each pressure, masses (in amu, q = –e assumed, average FC2 current given in brackets) 32 (30 pA), 34 (15 pA), 35 (155 nA), 36 (15 pA), and 37 (53 nA) were monitored at FC2, and the AMS system was set for detection of the respective mass X$^-$ $\rightarrow$ X$^{+3}$ signal. In this way, ion source stability and the levels of $^{32}\text{S}^-$, $^{34}\text{S}^-$, $^{35}\text{Cl}^-$, m = 36 anions and $^{37}\text{Cl}^-$ could be monitored.

Above 9 mTorr, accumulation times of 1000 s for $^{34}\text{S}$ and m = 36 amu, and 500 s for $^{32}\text{S}$ were used. From 6 – 9 mTorr, times of 500 s for $^{34}\text{S}$ and m = 36 amu, and 200 s for $^{32}\text{S}$ were used. From 2 – 5.5 mTorr, times of 300 s for $^{34}\text{S}$ and m = 36 amu, and 100 s for $^{32}\text{S}$ were used. Below these pressures, either the rate meter or the Faraday cup was used.

The $^{32}\text{S}^-$ and $^{34}\text{S}^-$ isotope attenuation data were used to calculate an expected contribution from $^{36}\text{S}^-$ to the mass 36 amu blank based on natural abundances of S ($^{32}\text{S} = 94.93\%$, $^{34}\text{S} = 4.29\%$ and $^{36}\text{S} = 0.02\%$ from Baum et al. (2002). This is plotted in Figure 11-1a) along with the m = 36 amu data. Data were otherwise not normalized or corrected and represent the raw signal detected at FC7. The $^{35}/^{37}\text{Cl}^-$ attenuations were consistent with Figure 10-1.
Figure 11-1: $^{36}$Cl/Cl $\sim 4 \times 10^{-11}$ Reference Standard Measured at $V_T = 1.75$ MV vs. NO$_2$ Pressure

The mass 36 amu peak and $^{32}$S$^-$ and $^{34}$S$^-$ attenuations for target Z93 – 0003 (Table 11.1) were measured versus collision cell NO$_2$ pressure. Typical settings were used (section 7.6) with the ion source at $-20$ kV, $\Delta V_{\text{ISAS}} = 12$ V and accelerator terminal voltage $V_T = 1.75$ MV for $X^- \to X^+$ detection at FC7. a) Shown is the $^{36}X^- \to ^{36}X^+$ signal versus pressure. The S data was used with the natural isotope abundances given in Baum at al. (2002) to calculate the expected $^{36}S^- \to ^{36}S^+$ signal, and the two sets of data agree very well. Also shown is the actual signal measured at 12 mTorr. b) Shown are ionization detector channel spectra at four pressures. The three peaks from $^{12}C^- \to ^{12}C^+$ interference can be seen, as discussed in sections 10.3.2 and 10.4.
Figure 11-1b) shows the ionization detector spectrum at 4 pressures. The first three peaks are partially due to the $^{12}\text{C}_3^-$ break-up in the stripping canal as discussed in section 10.3.2 and shown in Figure 10-11. The $^{12}\text{C}^+$ peak also coincides with a carbon peak from a continuum of ions from residual carbon in the stripping canal. The $3(^{12}\text{C})^+$ peak slightly overlaps the $^{36}\text{Cl}^+^3 + ^{36}\text{S}^+^3$ peak but the two peaks were resolved by the final detector because the ion energies were below the Bragg peak (see bullet 3, section 10.3.2). From Figure 10-11, the $3\text{C}^+$ peak should have been 1 order of magnitude below the $2\text{C}^+$ peak with the settings used, representing a negligible contribution to the $^{36}\text{Cl}^+^3$ signal at higher pressures.

11.2 $^{36}\text{Cl}$ Reference Material Measurements

This section discusses the $^{36}\text{Cl}/\text{Cl}$ measurements for all targets in Table 11.1. The collision cell with gradient bars and $\phi3$ mm apertures L2 – L5 (Figure 7-4) had been installed and all data were taken using typical settings (section 7.6) with the ion source at $-20.7$ kV, $\Delta V_{\text{ISAS}} = 4$ V (Eq 7.1), and $V_T = 1.75$ MV for stripping to $q = +3$. Prior to measurement, the ion source was thoroughly cleaned and the base ISA chamber pressure $P_{\text{ISA}} < 1 \times 10^{-7}$ Torr.

Based on the observed attenuations of $\text{S}^-$ and $\text{C}_3^-$ (see chapter 10), a collision cell pressure of 8 mTorr NO$_2$ was maintained during $^{36}\text{Cl}^-$ measurements. This was also the ‘plateau’ region of the curves (eg section 10.3.5) so that small pressure fluctuations should not have resulted in large signal fluctuations. Tuning for ISA settings was done with 35 nA of $^{35}\text{Cl}^-$ (FC2), achieving FC2 to FC7 transmissions of ~ 4% at base pressure and ~ 1% at 8 mTorr NO$_2$. The relatively low base pressure transmission, as compared to those in Table 10.3 for example, was due to the low value of $\Delta V_{\text{ISAS}}$. The issue has been discussed in chapter 8 (eg Figure 8-1).

11.2.1 Background

The m/q = 36 beam injected into the ISA was typically in the range 30 – 70 pA at FC2. A voltage offset $\Delta V_{\text{ISAS}} = 4$ V was used with 8 mTorr NO$_2$ in the collision cell and the AMS system was set for $^{36}\text{Cl}^- \rightarrow ^{36}\text{Cl}^+^3$ detection at $V_T = 1.75$ MV. Ionization detector signal accumulation times are given in the next section but did not exceed 900 s for any measurement. The minimum signal observed was 8 c / 900 s for a $^{36}\text{Cl}^- \rightarrow ^{36}\text{Cl}^+^3$ measurement with 8 mTorr NO$_2$ in the cell, above any observed background in this section.

Prior to these measurements, the test bed, ISA and AMS system were warmed up over a period of 2 days, and target Z93 – 0006 was used to assess the background. As discussed in
section 11.1.1, since Ar was used as the stripping gas at the accelerator terminal, there was possibility of a $^{36}\text{Ar}^{+3}$ contribution to the blank. Furthermore, as discussed in section 10.3.5 and regarding the cause of the S$^-$ + NO$_2$ attenuation plateau, contributions from ‘fast neutrals’, reactions or ionization of NO$_2$ and residual gas impurities leading to background for the $^{36}\text{Cl}^-$ measurement were considered. The following background sources were investigated after ISA tuning with $\Delta V_{\text{ISAS}} = 4$ V and 8 mTorr NO$_2$ in the collision cell. The AMS system was set for $^{36}\text{Cl}^- \rightarrow ^{36}\text{Cl}^{+3}$ detection using $V_T = 1.75$ MV.

Background from the Ar gas in the accelerator stripping column and NO$_2$ impurities with no ion beam transmission was tested first. With FC1 in the path of the ion beam, there were 0 counts on peak ($q = +3$) over an accumulation time of 2300 s.

Next, background from ionization of NO$_2$ impurities and Ar gas in the accelerator stripping column with ion injection was tested. A 1.6 pA beam of $^{34}\text{S}^-$ ($m/q = 34$ at FC2) was injected into the ISA and no signal was detected on peak over 1600 s. Then 23 pA of $^{32}\text{S}^-$ ($m/q = 32$ at FC2, similar in intensity to the $m/q = 36$ beams used for $^{36}\text{Cl}$ analyses) was injected into the ISA and 0 counts were detected on peak in 1556 s.

Although there would have been very little S$^-$ emanating from the ISA at 8 mTorr NO$_2$ pressure, the NO$_2^-$ signal would have been on the order of 1% of the original S$^-$ signal, and there may have been significant levels of other NO$_2^-$ + NO$_2$ reaction products (see Figure 10-10 and associated discussion). There is no energy or mass filtration between the ISA exit and accelerator injection so that reaction products would have entered the stripping canal. In this way, injection of S$^-$ not only tested accelerator background under experimental conditions, but also tested for Ar ionization while injecting anions.

On the other hand, this also means that the $^{36}\text{S}^- + \text{NO}_2$ reaction products containing $^{36}\text{S}$ are also potential sources of background for $^{36}\text{Cl}$ analyses. This has been discussed in section 11.1.1. Again, the measurements of this section suggest that the background from reaction products was well below the peaks observed during the $^{36}\text{Cl}$ measurements of this section.

Background that possibly originates from ‘fast neutrals’ or ‘fast ions’ has been discussed in section 10.3.5.1. The quadrupole just before the collision cell and following lens were set to RFQ2 DC = L2 = –200 V (see Figure 7-4) in order to reflect low energy ions before entry into the collision cell. Then, $m/q = 36$ was injected into the ISA (15 pA at FC2). No signal was observed on peak over 1600 s accumulation time. The measurement was repeated with target
Z93 – 0003 (largest $^{36}$Cl abundance) with $L1 = RFQ1 \ DC = -700$ V and $RFQ2 \ DC = L2 = -200$ V and no signal was observed on peak over 1800 s.

A blank AgCl sample was not included with the $^{36}$Cl reference standards, but the $^{32}$S$^{-}$ signal from target Z93 – 0006 was used to gather an estimate of the $^{36}$S$^{-}$ background. Ion source conditions were set for large anion beam production and a scan of the test bed magnet yielded the following at FC2: 280 nA of $^{37}$Cl$^{-}$, 950 nA of $^{35}$Cl$^{-}$, 74 pA at $m/q = 32$, giving a ratio $S/Cl \leq 6 \times 10^{-5}$ (assuming $^{32}$S = 94.93% of S and $^{35}$Cl = 75.78% of Cl as in Baum et al. 2002).

Injecting 60 pA $^{32}$S$^{-}$ into the ISA at base pressure gave an FC7 $^{32}$S$^{+3}$ signal of 2.05 pA (not all of the signal at $m/q = 32$ was from $^{32}$S$^{-}$, other contributions could have come from $^{16}$O$_2$ for example). Injecting 34 pA $^{32}$S$^{-}$ into the ISA with 8 mTorr NO$_2$ gave an FC7 $^{32}$S$^{+3}$ signal of 135 c / 100 s for a relative $S^{-}$ attenuation of $5.6 \times 10^{-7}$, consistent with the expected attenuation (eg Figure 10-8). Then, the $^{36}$S$^{-} \rightarrow^{36}$S$^{+3}$ level relative to the $^{35}$Cl$^{-} \rightarrow^{35}$Cl$^{+3}$ should be $^{36}$S$^{+3}$/$^{35}$Cl$^{+3} \leq 8.9 \times 10^{-15}$ (assuming $^{36}$S = 0.02% of S, ibid). This background is more than an order of magnitude below the lowest $^{36}$Cl/Cl ratio reference standard measured.

### 11.2.2 Results

Raw data from the $^{36}$Cl/Cl ratio measurements of the four reference standards (Table 11.1) are given in Table 11.2. The $^{35}$Cl$^{-}$ signal was measured at FC2 and was typically between 140 and 400 nA, although currents up to 875 nA were also used. Then the $m/q = 36$ beam (typically in the range 30 – 70 pA at FC2) was injected into the ISA at 8 mTorr NO$_2$ pressure and the resulting $^{35}$Cl$^{-} \rightarrow^{35}$Cl$^{+3}$ signal measured using the ionization detector, monitoring the $q = +3$ channel (example spectra can be seen in Figure 11-1). Stripping was conducted with an accelerator terminal voltage of $V_T = 1.75$ MV. Transmission of $^{35}$Cl$^{-}$ from FC2 to FC7 for $^{35}$Cl$^{+3}$ detection at 8 mTorr NO$_2$ pressure was on the order of 1% so that the FC2 signal should be corrected when calculating $^{36}$Cl/Cl ratios with these data.

A minimum of 10 ratio measurements were made for each target. With $N$ the number of $^{36}$Cl$^{+3}$ counts at the ionization detector over the measurement interval, the statistical uncertainty of each measurement was calculated using $\sqrt{N}$ for $N \geq 9$ and 3 for $N < 9$. Because of ISA instabilities, counting times were limited for many of the measurements, leading to rather large uncertainties in the counting statistics. Many of the instability problems have been addressed since these measurements and another set of measurements should yield better data. On the other
hand, due to the rather poor transmission of the ISA, relatively long counting times were needed for the lower \(^{36}\text{Cl}/\text{Cl}\) abundance targets.

Calculations of \(^{36}\text{Cl}/\text{Cl}\) ratios from this data are given in Table 11.3 and compared to the accepted values as given by PRIME Lab. The measured ratio was calculated using a weighted average of the data in Table 11.2 as follows. The \(^{35}\text{Cl}^-\) signal was divided by 0.7578 to account for Cl abundance (as given in Baum et al. 2002) and multiplied by 0.01 to account for FC2 to FC7 transmission (see first paragraph of this section). Let this value be \(I_{35}\), and let \(I_{36}\) be the corresponding \(^{36}\text{Cl}^+\) count rate. Let the prefix ‘d’ denote measurement uncertainties so that \(dI_{35}/I_{35} = 3\%\) and \(dI_{36} = \sqrt{N}/t\) or \(3/t\) (\(t\) is the counting time, this is the statistical uncertainty discussed in the last paragraph). Finally, let \(I = I_{36}/I_{35}\) so that \(I\) has uncertainty

\[
dI = I \cdot \sqrt{\frac{dI_{36}^2}{I_{36}^2}} + 0.0009\ .
\]

Weighted averages for the measured \(^{36}\text{Cl}/\text{Cl}\) ratio of each target were then calculated by

\[
\left(\sum \left(\frac{1}{(dI)^2}\right)\right)^{-1}, \left(\sum (dI)^{-2}\right)^{-1}.
\]

More information can be found in Bevington (1969).

These weighted averages were also normalized to the PRIME Lab reference value for target Z93 – 0003, and this is plotted in Figure 11-2. A linear regression was applied to the data and the line of fit is presented with associated statistics. Also shown is the anticipated \(^{36}\text{S}\) background level as calculated at the end of section 11.2.1.

### 11.3 Discussion

Figure 11-1 and Figure 11-2 provide clear demonstrations of the effectiveness of using gas-phase ion reactions at low energy for isobar separation before abundance ratio measurements by AMS. With the current test bed and ISA, the \(^{36}\text{S}^-\) levels as shown in Figure 11-1 and calculated in section 11.2.1 from a target with S/Cl \(\leq 6 \times 10^{-5}\) corresponds to a \(^{36}\text{Cl}/\text{Cl}\) abundance limit of \(9 \times 10^{-15}\) using a terminal voltage of 1.75 MV for detection of \(^{36}\text{Cl}^+\). In Figure 11-1 and Figure 10-11, and as discussed in section 10.6, the added attenuation of the \(^{12}\text{C}_3^-\) contribution under these measurement conditions has also been seen to be large.

From Table 11.3, the weighted average \(^{36}\text{Cl}/\text{Cl}\) ratios from the four \(^{36}\text{Cl}\) standards were within 18%, 0.2%, 6%, and 13% of the reference values, rather encouraging considering the ISA
instability problems and other measurement difficulties (including having to manually adjust Faraday cups and monitor gas pressure). Instabilities have improved and are currently being addressed. The ratios between measured and reference values ranged from 0.88 to 1.2 which is within the range of transmission fluctuations, 0.9% - 1.1% from FC2 to FC7. Because the $^{35}$Cl signal was measured at FC2 while the $^{36}$Cl signal was measured at FC7, the $^{35}$Cl data did not reflect FC2 to FC7 transmission fluctuations while the $^{36}$Cl data did.

Precision and accuracy would be improved with improved ISA transmission and collision cell gas pressure stability. With increased transmission, shorter data accumulation times can be used, decreasing effects from system variability and improving counting statistics. Transmission has already been addressed extensively in this thesis. For the less massive anions, introduction of a cooling cell that used a less massive cooling gas (such as CH$_4$) before introduction to an NO$_2$ reaction cell could greatly improve transmission. Also, wider entrance apertures at the initial collision cell entrance would accommodate larger ion beam energy spreads. This may be facilitated by using a longer cell at lower pressure so that adequate differential pumping could be maintained. With 1% FC2 to FC7 transmission, if a $^{36}$Cl$^- \rightarrow ^{36}$Cl$^{+3}$ count rate of 1 c/s were to be measured from a $^{36}$Cl/Cl $= 10^{-15}$ sample, 16 mA Cl$^-$ would need to be generated, and a 270 $\mu$A beam of Cl$^-$ would yield 1 c/min $^{36}$Cl signal.

As discussed in sections 11.1.1 and 11.2.1, there were no mass or energy discriminators between the ISA and accelerator so that all ions exiting the ISA, including reaction products, were potentially injected into the stripping canal. Any reaction products that contained $^{36}$S were potential sources of background. For example, the $S^- + NO_2 \rightarrow NSO_2^- \rightarrow NSO_2$ level in Figure 10-10 was more than one order of magnitude above the $S^-$ signal at higher pressures. However, like Ar ionized in the stripping canal, contributions from NSO$_2^-$ break-up to $^{36}$S would be suppressed by the subsequent electric and magnetic analyzers because of the remaining kinetic energy after break-up. Such background could be reduced by addition of mass discrimination after the collision cell, for example an rf quadrupole mass filter between the cell and re-acceleration stage of the ISA.

Nonetheless, the measured and reference $^{36}$Cl data plot well against one-another linearly in Figure 11-2. Combined with the background measurements (sections 11.1.1 and 11.2.1) and results from Figure 11-1, these results show that the rf quadrupole accelerator mass spectrometry (RFQ–AMS) technique applied to isobar separation is currently scalable over at least 2 orders of magnitude. Furthermore, the relative $^{37}$Cl$^-$ and $^{32}$S$^-$ attenuation shown in Figure 10-9 measured
using \( V_T = 1 \) MV for stripping to \( q = +1 \) was the same as that measured using the \( q = +3 \) charge state at \( V_T = 1.75 \) MV (see also Figure 10-8). There is, then, indication that with an improved ISA, RFQ–AMS could make \(^{36}\text{Cl}\) analyses possible on smaller AMS systems (\( \leq 1 \) MV).

Assessment of the true \(^{36}\text{Cl}^+\) background and measurement of the \(^{36}\text{Cl}\) standards using 1 MV accelerator terminal voltage with the current test bed and ISA would be useful in the near future.

**Figure 11-2: Four \(^{36}\text{Cl}/\text{Cl}\) Reference Standard Ratios Measured at 1.75 MV with the ISA**

Compared to the Reference Values from PRIME Lab

![Graph showing measured \(^{36}\text{Cl}/\text{Cl}\) ratios against reference values from PRIME Lab. The graph includes a linear fit with the following details:

- **Slope:** 1.0314 ± 0.0138
- **Correlation Coefficient:** 0.9998
- **Standard Deviation:** 0.9968

Ratios from the reference \(^{36}\text{Cl}\) standards listed in Table 11.1 measured using the ISA and IsoTrace Lab AMS system are compared to the reference values from PRIME Lab. Data was taken with the ion source set at \(-20.7\) kV, \( \Delta V_{\text{ISAS}} = 4 \) V and 8 mTorr \( \text{NO}_2 \) ISA collision cell pressure, using typical settings (section 7.6) with the accelerator terminal voltage set at \( V_T = 1.75 \) MV for measurement of \(^{36}\text{Cl}^- \rightarrow ^{36}\text{Cl}^{+3}\). Each \(^{36}\text{Cl}/\text{Cl}\) ratio was taken a minimum of 10 times. Points represent a weighted average of the measurements, normalized to the PRIME Lab reference value for target Z93–0003. Values are given in Table 11.3 and raw data is presented in Table 11.2.
Table 11.2: Raw Data from $^{36}$Cl Reference Standard Measurements (caption on p. 11—212)

<table>
<thead>
<tr>
<th>$^{36}$Cl/Cl = $4.18 \times 10^{-11}$ (target Z93 – 0003)$^a$</th>
<th>$^{36}$Cl/Cl = $4.42 \times 10^{-12}$ (target Z93 – 0004)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{35}\text{Cl}^{-} \ (^{37}\text{Cl})$ at FC2$^b$</td>
<td>$^{35}\text{Cl}^{-} \ (^{37}\text{Cl})$ at FC2$^b$</td>
</tr>
<tr>
<td>(nA ± 3%)</td>
<td>(nA ± 3%)</td>
</tr>
<tr>
<td>$^{36}\text{Cl}^{\text{I}+3}$ (at FC7)$^c$</td>
<td>$^{36}\text{Cl}^{\text{I}+3}$ (at FC7)$^c$</td>
</tr>
<tr>
<td>counts</td>
<td>counts</td>
</tr>
<tr>
<td>time (s)</td>
<td>time (s)</td>
</tr>
<tr>
<td>155</td>
<td>270</td>
</tr>
<tr>
<td>165 (46)</td>
<td>265</td>
</tr>
<tr>
<td>180 (54)</td>
<td>210</td>
</tr>
<tr>
<td>200 (60)</td>
<td>200 (59)</td>
</tr>
<tr>
<td>205 (62)</td>
<td>200 (58)</td>
</tr>
<tr>
<td>210 (62)</td>
<td>190 (55)</td>
</tr>
<tr>
<td>210 (59)</td>
<td>160 (46)</td>
</tr>
<tr>
<td>225 (63)</td>
<td>160 (47)</td>
</tr>
<tr>
<td>200 (59)</td>
<td>155 (44)</td>
</tr>
<tr>
<td>200</td>
<td>155 (44)</td>
</tr>
<tr>
<td>210</td>
<td>143 (39)</td>
</tr>
<tr>
<td>205</td>
<td>160 (47)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$^{36}$Cl/Cl = $1.20 \times 10^{-12}$ (target Z93 – 0005)$^a$</th>
<th>$^{36}$Cl/Cl = $4.08 \times 10^{-13}$ (target Z93 – 0006)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{35}\text{Cl}^{-} \ (at \ FC2)^b$</td>
<td>$^{35}\text{Cl}^{-} \ (at \ FC2)^b$</td>
</tr>
<tr>
<td>(nA ± 3%)</td>
<td>(nA ± 3%)</td>
</tr>
<tr>
<td>$^{36}\text{Cl}^{\text{I}+3}$ (at FC7)$^c$</td>
<td>$^{36}\text{Cl}^{\text{I}+3}$ (at FC7)$^c$</td>
</tr>
<tr>
<td>counts</td>
<td>counts</td>
</tr>
<tr>
<td>time (s)</td>
<td>time (s)</td>
</tr>
<tr>
<td>295</td>
<td>740</td>
</tr>
<tr>
<td>295</td>
<td>680</td>
</tr>
<tr>
<td>560</td>
<td>700</td>
</tr>
<tr>
<td>520</td>
<td>875</td>
</tr>
<tr>
<td>470</td>
<td>720</td>
</tr>
<tr>
<td>440</td>
<td>155</td>
</tr>
<tr>
<td>390</td>
<td>140</td>
</tr>
<tr>
<td>290</td>
<td>740</td>
</tr>
<tr>
<td>290</td>
<td>620</td>
</tr>
<tr>
<td>330</td>
<td>470</td>
</tr>
</tbody>
</table>
a) Refer to Table 11.1 for more target information.

b) The $^{35}\text{Cl}^-$ signal was monitored at FC2, not FC7, and $^{37}\text{Cl}^-$ was likewise monitored periodically (given in brackets beside the $^{35}\text{Cl}^-$ data) for two targets. Transmission FC2 to FC7 was ~1% with slight fluctuation over the course of measurements. Consideration should be given to this for ratio calculations.

c) This was the signal from the ionization detector channel for $q = +3$ with the AMS system set for $^{36}\text{Cl}^- \rightarrow ^{36}\text{Cl}^+^3$ at $V_T = 1.75$ MV, more information can be found in Figure 11-1 and related discussions. The columns give the signal accumulation time in seconds and the number of counts recorded. If $N$ represents the number of counts, the statistical uncertainty of each measurement was taken to be $\sqrt{N}$ for $N \geq 9$ and 3 for $N < 9$. Typically the FC2 $m/q = 36$ signal was 30 – 70 pA and 8 mTorr NO$_2$ was used in the collision cell with $\Delta V_{\text{ISAS}} = 4$ V.

Table 11.3: $^{36}\text{Cl}/\text{Cl}$ Measured Ratios

<table>
<thead>
<tr>
<th>Target ID$^a$</th>
<th>$^{36}\text{Cl}/\text{Cl}$ Accepted Ratio$^a$</th>
<th>$^{36}\text{Cl}/\text{Cl}$ Measured Ratio$^b$</th>
<th>Difference$^c$ (%)</th>
<th>Accepted to Measured Ratio$^d$</th>
<th>$^{36}\text{Cl}/\text{Cl}$ Measured Ratio Normalized to the Accepted Ratio$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z93 – 0003</td>
<td>4.16 x 10$^{-11}$</td>
<td>4.70 ± 0.10 x 10$^{-11}$</td>
<td>13</td>
<td>0.885</td>
<td>4.16 ± 0.09 x 10$^{-11}$</td>
</tr>
<tr>
<td>Z93 – 0004</td>
<td>4.42 x 10$^{-12}$</td>
<td>4.43 ± 0.22 10$^{-12}$</td>
<td>0.2</td>
<td>0.998</td>
<td>3.92 ± 0.02 10$^{-12}$</td>
</tr>
<tr>
<td>Z93 – 0005</td>
<td>1.20 x 10$^{-12}$</td>
<td>0.980 ± 0.090 x 10$^{-12}$</td>
<td>18</td>
<td>1.225</td>
<td>0.867 ± 0.008 10$^{-12}$</td>
</tr>
<tr>
<td>Z93 – 0006</td>
<td>4.08 x 10$^{-13}$</td>
<td>4.30 ± 0.34 x 10$^{-13}$</td>
<td>5.4</td>
<td>0.949</td>
<td>3.81 ± 0.30 x 10$^{-13}$</td>
</tr>
</tbody>
</table>

a) $^{36}\text{Cl}$ reference standards were from PRIME Lab, more information can be found in Table 11.1.
b) This represents a weighted average of the data for each target listed in Table 11.2. The $^{35}\text{Cl}^-$ signal has been divided by 0.7574 to account for the isotope abundance (as in Baum et al. 2002) and multiplied by 0.01 to account for the average FC2 to FC7 transmission ($^{36}\text{Cl}$ was measured at FC7, $^{35}\text{Cl}$ at FC2).
c) Calculated by: $[(\text{accepted value} - \text{measured value})/\text{accepted value}] \times 100\%$.
d) Calculated by: $(\text{accepted value})/(\text{measured value})$
e) Measured values were normalized to the Z93 – 0003 ratio and then multiplied by the Z93 – 0003 accepted value.
12 Isobar Suppression for $^{90}$Sr Analyses: $\text{SrF}_3^-$, $\text{YF}_3^-$ and $\text{ZrF}_3^-$ + NO$_2$ Attenuations and Reactions

At this stage it is well beyond the scope of this already lengthy thesis to present very detailed analyses of more anion–gas reactions studied with the ISA. However, it is useful to present some attenuation data regarding possible future $^{90}$Sr analysis with reaction curves that have been measured as a guide for possible future work and directions.

The only known stable atomic isobar for $^{90}$Sr ($t_{1/2} = 28.78$ years) is $^{90}$Zr (52% of Zr), and the only other atomic isobar with $t_{1/2} > 1$ day is $^{90}$Y ($t_{1/2} = 2.67$ days, as compiled in Baum et al. 2002). Typically Cs$^+$ sputter anion production rates are relatively low for these elements as atomic anions, which have electron affinities of $\text{EA(Sr)} = 0.048$ eV, $\text{EA(Y)} = 0.307$ eV and $\text{EA(Zr)} = 0.426$ eV (as compiled by Haynes and Lide 2011). However, use of sufficient amounts of PbF$_2$ powder in the sputter target matrix has been found to boost fluoride molecular anion production of the form $\text{MF}_n^-$ (M an element, n an integer) when the resulting molecular anion has large electron affinity (Zhao et al. 2010a).

The number of F atoms, n, depends on the elemental nature of M. This ‘matrix assisted’ method not only facilitates anion beam production of elements that have relatively weak electron affinities by use of a fluoride molecular anion carrier, but can also facilitate isobar suppression at the ion source when n is different for the isobars. For the isobars under study, n = 3 for Sr, n = 4 for Y and n = 5 for Zr (as might be expected from their valencies). Relative sputtering efficiencies have been measured as $\text{SrF}_3^-/\Sigma\text{SrF}_n^- \sim 99.9\%$, $\text{YF}_3^-/\Sigma\text{YF}_n^- \sim 0.002\%$, $\text{ZrF}_3^-/\Sigma\text{ZrF}_n^- \sim 0.003\%$, suggesting isobar suppression on the order of $10^{-5}$ at the ion source when using $\text{SrF}_3^-$. 

Because of the low anion sputter production rate, YF$_3$ and ZrF$_3$ were thought to have weak electron affinities, while SrF$_3$ to have a strong electron affinity because of the large production rate. Relative attenuations in the ISA using NO$_2$ were then studied.

12.1 $\text{SrF}_3^-$, $\text{YF}_3^-$, $\text{ZrF}_3^-$ + NO$_2$ Attenuations

$\text{SrF}_3^-$, $\text{YF}_3^-$ and $\text{ZrF}_3^-$ attenuations in NO$_2$ are presented in Figure 12-1. The ion source deck voltage had to be raised to $V_s = -15$ kV (typically $-20$ kV was used) because of the limited
field available from the test bed magnet, but the target was still held at –4 kV for Cs⁺ sputter acceleration. An accelerator terminal voltage of $V_T = 1.2$ MV was used for MF₃⁻ $\rightarrow$ M⁺² with $\Delta V_{ISAS} = 5.3$ V (Eq 7.1) while $V_T = 1.9$ MV with $\Delta V_{ISAS} = 4.8$ V for MF₃⁻ $\rightarrow$ M⁺³. Otherwise, typical settings (section 7.6) were used. When signals fell below 1000 c/s, ionization detector signal accumulation times of 100 s were used. For $\Delta V_{ISAS} = 5.3$ V measurements, $q_2 = 0.07$ and for $\Delta V_{ISAS} = 4.8$ V measurements, $q_2$ ranged from 0.12 to 0.14. Other relevant information, such as ISA injection currents and sputter target materials, is summarized in Table 12.1 below.

Transmissions of 90% from FC2 to FC3 had been measured for SrF₃⁻ under these conditions. As described in section 12.2 regarding stripping yield corrections for ZrF₃⁻, the SrF₃⁻ $\rightarrow$ Sr⁺³ yield should be close to 10%. However, FC2 to FC7 transmission was only 1%. Even accounting for the FC3 to FC4 transmission losses particular to the current test bed and AMS system coupling (see section 8.1.4), this is rather low and is likely an indication that most of the FC2 signal was not $^{88}$SrF₃⁻.

Table 12.1: Sputter, Kinetic Energy and Transmission Data for SrF₃⁻, YF₃⁻ and ZrF₃⁻ in NO₂

<table>
<thead>
<tr>
<th>Sputter Target Material (ratio by volume)</th>
<th>Anion</th>
<th>$\Delta V_{ISAS}$ (Eq 7.1) [eV]</th>
<th>$K_R$ [eV]</th>
<th>FC2ᵃ [nA]</th>
<th>Base Pisa (x 10⁻⁷ Torr)</th>
<th>FC7 / FC2ᵃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrF₄ + PbF₂ (1:10)</td>
<td>$^{90}$SrF₃⁻</td>
<td>5.3</td>
<td>1.26</td>
<td>0.145</td>
<td>1.1</td>
<td>2.6ᵇ</td>
</tr>
<tr>
<td>SrF₂ + ZrF₄ + PbF₂ (1:1:10)</td>
<td>YF₃⁻</td>
<td>4.8</td>
<td>1.14</td>
<td>0.065</td>
<td>1.1</td>
<td>1.3ᵇ</td>
</tr>
<tr>
<td>YF₃ + PbF₂ (1:5)</td>
<td>$^{89}$YF₃⁻</td>
<td>5.3</td>
<td>1.27</td>
<td>6.4</td>
<td>1.1</td>
<td>2.9ᵇ</td>
</tr>
<tr>
<td>SrF₂ + ZrF₄ + PbF₂ (1:1:10)</td>
<td>$^{88}$SrF₃⁻</td>
<td>4.8</td>
<td>1.16</td>
<td>10</td>
<td>1.1</td>
<td>1.9ᵇ</td>
</tr>
</tbody>
</table>

a) The majority of the FC2 signal was not necessarily due to the analyte anion. Even though the FC2 to FC7 transmission was relatively low, base pressure FC2 to FC3 transmission for $^{88}$SrF₃⁻ was 90%.
b) Detection was XF₃⁻ $\rightarrow$ X⁺² with $V_T = 1.2$ MV
c) Detection was XF₃⁻ $\rightarrow$ X⁺³ with $V_T = 1.9$ MV

The ion source was set to –15 kV due to limitations imposed by the maximum field of the test bed magnet. With the further exceptions in notes a) and b), measurements were made using typical settings (section 7.6, 4 keV Cs⁺ sputtering).
Figure 12-1: SrF$_3^-$, YF$_3^-$ and ZrF$_3^-$ Relative Total Attenuations in NO$_2$ with $\Delta V_{\text{ISAS}} < 5.5$ V

Targets were sputtered by 4 keV Cs$^+$ and accelerated to 15 keV for mass analysis. For MF$_3^-$ $\rightarrow$ M$^{+2}$ data, an accelerator terminal voltage of $V_T = 1.2$ MV was used with $\Delta V_{\text{ISAS}} = 5.3$ V. For MF$_3^-$ $\rightarrow$ M$^{+3}$, $V_T = 1.9$ MV with $\Delta V_{\text{ISAS}} = 4.8$ V. More information such as injection currents for the ISA (at FC2), target materials, and FC2 to FC7 transmission at base pressure can be found in Table 12.1. For signals below 1000 c/s, an ionization detector signal accumulation time of 100 s was used.

12.2 ZrF$_3^-$ + NO$_2$ Reaction Channels

The attenuation cross section of ZrF$_3^-$ in NO$_2$ was the largest of all those observed with the ISA, 1.95 x $10^{-14}$ cm$^2$ (see section 12.4). An attempt was made to determine which reaction channels gave rise to the losses.

Figure 12-2 shows the results of measurements of ZrF$_3^-$ $\rightarrow$ NO$_2$ $\rightarrow$ ZrOF$_3^-$, ZrO$_2$F$^-$ and NO$_2^-$ and ZrF$_3^-$ attenuation in air using the conditions outlined in section 12.1 for $^{90}$ZrF$_3^-$ $\rightarrow$ $^{90}$Zr$^{+3}$ with $V_T = 1.9$ MV and $\Delta V_{\text{ISAS}} = 4.8$ V. Signals for the curves involving ZrX$^-$ were
monitored using the $^{90}\text{Zr}^{+3}$ fragment at FC7 while the NO$_2^-$ signal was monitored using the $^{14}\text{N}^+$ fragment at FC7, all using $V_T = 1.9$ MV for stripping. Signals were confirmed by ionization detector spectra for the F$^+$ fragments for Zr$^{+3}$ and O$^+$ fragments for N$^+$.

Electron stripping yields for Zr in Ar versus kinetic energy have not been found, but some stripping correction was needed in order to reasonably compare the data (see section 7.7). From Wittkower and Betz (1973), the Br$^{+3}$ stripping yield is 16.4% in Ar at 2 MV, Kr$^{+3}$ is 7.75% at 0.8 MV and I$^{+3}$ is 10.7% at 1.05 MV. In the present case, the mass ratio of Zr/ZrF$_3$ is 0.61 so that there was a stripping energy of 1.2 MV. A stripping yield on the order of 10% for $^{90}\text{ZrF}_3^- \rightarrow ^{90}\text{Zr}^{+3}$ has been assumed. On the other hand, the stripping efficiency for N$^+$ in Ar at 0.6 MV is 52.8% (ibid). In order to compare the ZrX$^-$ yields to the NO$_2^-$ yields, the N$^+$ signal has been divided by 5 to account for stripping efficiency. No correction was applied to the Zr$^{+3}$ yields from different parent molecules.

An accelerator terminal voltage scan (‘$V_T$ scan’) was also used to search for ZrF$_3^-$ + NO$_2\rightarrow$ ZrX$^-$ → (AMS) Zr$^{+2}$ reaction products with 0.6 mTorr NO$_2$ in the collision cell. This technique has already been described in sections 7.7 and 10.3. Briefly, $V_T$ was scanned while the rest of the high energy AMS system was set for a specific m/q fragment. Parent molecule masses could be calculated based on the voltage that the fragment signal was observed.

Conditions were the same as those outlined in section 12.1 for $^{90}\text{ZrF}_3^- \rightarrow ^{90}\text{Zr}^{+2}$ with $\Delta V_{\text{ISAS}} = 5.3$ V (see Table 12.1 and caption to Figure 12-1) but using $V_T = 1.27$ MV for $^{90}\text{ZrF}_3^- \rightarrow ^{90}\text{Zr}^{+2}$ stripping and injecting 82 pA for m/q = 147 ($^{90}\text{Zr}^{19}\text{F}_3^-$) into the ISA. The electron transfer channel ZrF$_3^-$ + NO$_2\rightarrow$ NO$_2^-$ was also observed using the $^{16}\text{O}^+$ stripping fragment with $V_T = 1.2$ MV.

A stripping correction for comparison of the ZrX$^-$ and NO$_2^-$ results was calculated based on data from Wittkower and Betz (1973) in a similar way as outlined for Figure 12-2. Stripping yields are given as: 42.9% for Br$^{+2}$ in Ar at 2 MV, 23.3% for Kr$^{+2}$ at 0.8 MV and 30% for I$^{+2}$ in Ar at 1.05 MV. A stripping yield on the order of 25% was assumed for $^{90}\text{ZrF}_3^- \rightarrow ^{90}\text{Zr}^{+2}$ at 1.3 MV. The stripping efficiency for N$^+$ in Ar was used as a proxy for O$^+$ (no correction for the 2O$^+$ add-up signal was made). Stripping efficiency for N$^+$ in Ar are given as 52.8% at 0.3 MV and 50.0% at 0.4 MV so that the O$^+$ stripping yield was assumed to be 50% and the O$^+$ datum was divided by 2. No correction was applied to the Zr$^{+2}$ yields from different parent molecules.

The consistency between the two sets of reaction product data and attenuations (Figure 12-1) using two different stripping charge states reinforces the reliability of the measurements.
For example, with the $q = +3$ charge state, ionization detector $q = +1$, $+2$ and $+3$ spectrum peaks would correspond to $m/q = 30$, 60 and 90, while for charge state $q = +2$ the correspondence would be $m/q = 45$, 90 and 135 respectively so that contributions to the background would not be likely from the same interference sources.

**Figure 12-2: ZrF$_3^-$ + NO$_2$ Reaction Channels with $\Delta V_{ISAS} = 4.8$ V**

Shown are some ZrF$_3^-$ + NO$_2$ reaction products and ZrF$_3^-$ attenuation in air with $\Delta V_{ISAS} = 4.8$ V. The ZrF$_3^-$ attenuation in air and ZrF$_3^-$ + NO$_2$ reaction products of the form ZrX$^-$ were monitored using the $^{90}$Zr$^{+3}$ stripping fragment with $V_T = 1.9$ MV and confirmed with the F$^+$ fragment spectra in the ionization detector. The NO$_2^-$ signal was monitored using $^{14}$N$^+$ after stripping at $V_T = 1.9$ MV and confirmed with an O$^+$ fragment spectrum. To account for stripping yield differences, the NO$_2^-$ data have been divided by 5. No correction has been applied to the Zr$^{+3}$ data from the various parent anions. Sputter target, injection current and other relevant information can be found in Table 12.1 under ZrF$_3^-$ with $\Delta V_{ISAS} = 4.8$ V, and settings can be found in the caption to Figure 12-1. All data were normalized to the respective base pressure ZrF$_3^-$ $\rightarrow$ Zr$^{+3}$ currents.
Table 12.2: ZrF$_3^-$ + NO$_2$ Reaction Channels with $\Delta V_{\text{ISAS}} = 5.3$ V

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Stripping Fragment</th>
<th>FC7 Signal</th>
<th>Signal Relative to $^{90}\text{ZrF}_3^-$ → $^{90}\text{Zr}^{+2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{90}\text{ZrF}_3^-$ + NO$_2$ → $^{90}\text{Zr}^{+2}$</td>
<td>Zr$^{+2}$</td>
<td>0.05 pA</td>
<td>156</td>
</tr>
<tr>
<td>$^{90}\text{ZrF}_3^-$</td>
<td>Zr$^{+2}$</td>
<td>2000 c/s</td>
<td>1</td>
</tr>
<tr>
<td>$^{90}\text{Zr}^{16}\text{O}^{19}\text{F}_3^-$</td>
<td>Zr$^{+2}$</td>
<td>200 c/s</td>
<td>0.1</td>
</tr>
<tr>
<td>$^{14}\text{N}^{16}\text{O}_2^-$</td>
<td>$^{16}\text{O}^+$</td>
<td>0.1 pA$^a$</td>
<td>312</td>
</tr>
</tbody>
</table>

a) This datum was divided by 2 to account for the relative Zr$^{+2}$ and O$^+$ stripping yields.

The accelerator terminal voltage was scanned (see text) for observation of $^{90}\text{ZrF}_3^-$ + NO$_2$ reaction products with 0.6 mTorr NO$_2$ pressure in the ISA and $\Delta V_{\text{ISAS}} = 5.3$ V, using $V_T = 1.27$ MV for $^{90}\text{ZrF}_3^-$ → Zr$^{+2}$. The NO$_2^-$ signal was detected with the O$^+$ fragment using $V_T = 1.2$ MV.

12.3 YF$_3^-$ + NO$_2$ Reaction Channels

While not as large as the ZrF$_3^-$ attenuation cross section in NO$_2$, YF$_3^-$ had a relatively large attenuation cross section of $7.6 \times 10^{-15}$ cm$^2$ (see section 12.4) compared to others studied with the ISA, slightly larger than for S$^-$ (see Table 10.8). Reaction channels were scanned using the ‘VT scan’ technique (see last section and sections 7.7 and 10.3) to search for $^{89}\text{YX}^-$ products over a mass range corresponding with $^{90}\text{Y}^{16}\text{O}^{19}\text{F}_3^-$ and $(^{90}\text{Y}^{19}\text{F}_3^-)^{14}\text{N}^{16}\text{O}_2$ at 1 mTorr NO$_2$ pressure while injecting 3.8 nA m/q = 146 ($^{89}\text{YF}_3^-$) into the ISA. Otherwise, conditions were the same as those outlined in section 12.1 for YF$_3^-$ with $\Delta V_{\text{ISAS}} = 5.3$ V. A terminal voltage of $V_T = 1.2$ MV was used for $^{89}\text{YF}_3^-$ → $^{89}\text{Y}^{+2}$ and product signals were monitored using the $^{89}\text{YX}^-$ → $^{89}\text{Y}^{+2}$ fragment. Only product signal peaks within 10% of the $^{89}\text{YF}_3^- \rightarrow ^{89}\text{Y}^{+2}$ signal (5 pA at 1 mTorr pressure) were recorded.

Under the same conditions, the reaction YF$_3^- +$ NO$_2 \rightarrow$ NO$_2^-$ was monitored versus NO$_2$ pressure using the $^{14}\text{N}^{16}\text{O}_2^- \rightarrow ^{16}\text{O}^+$ fragment with $V_T = 1.2$ MV for detection. A stripping yield of 25% was assumed for $^{89}\text{YF}_3^- \rightarrow ^{89}\text{Y}^{+2}$ and 50% for $^{14}\text{N}^{16}\text{O}_2^- \rightarrow ^{16}\text{O}^+$ based on the same considerations as described for the $^{90}\text{ZrF}_3^- \rightarrow ^{90}\text{Zr}^{+2}$ measurements of the last section, and the NO$_2^-$ data was divided by 2.

All data were normalized to the base pressure signal for $^{89}\text{YF}_3^- \rightarrow ^{89}\text{Y}^{+2}$ for comparison with the $^{89}\text{YF}_3^- +$ NO$_2$ attenuation data presented in Figure 12-1. The results are presented in Figure 12-3.
Figure 12-3: $^{89}\text{YF}_3^-$ + NO$_2$ Reaction Channels with $\Delta V_{\text{ISAS}} = 5.3$ V

Shown are some $^{90}\text{YF}_3^-$ + NO$_2$ reaction products observed while injecting 3.8 nA m/q = 146 (at FC2, $^{89}\text{YF}_3^-$) into the ISA with $\Delta V_{\text{ISAS}} = 5.3$ V. The $\text{YF}_3^-$ + NO$_2$ attenuation measurement has already been described for Figure 12-3. Besides the ISA injection current, conditions for the reaction product measurements described here were the same. Products of the form $^{90}\text{YX}^-$ were detected using the $^{89}\text{Y}^{+2}$ stripping fragment during a ‘VT scan’ (refer to text) at 1 mTorr cell pressure. Only peaks $\geq 10\%$ of the 1 mTorr $^{90}\text{YF}_3^- \rightarrow ^{90}\text{Y}^{+2}$ signal (5 pA) were recorded. The NO$_2^-$ signal was monitored using $^{16}\text{O}^+$ after stripping at $V_T = 1.2$ MV. To account for stripping yield differences, the NO$_2^-$ data have been divided by 2. No correction has been applied to the $\text{Y}^{+2}$ data from the various parent anions. All measurements were normalized to the respective base pressure $^{89}\text{YF}_3^- \rightarrow ^{89}\text{Y}^{+2}$ currents.

12.4 Cross Section Estimates

Cross section and reaction rate coefficient calculation methods have been discussed in section 10.5. Upper limits to the attenuation cross sections for YF$_3^-$ and ZrF$_3^-$ in NO$_2$ were calculated from the slopes in Figure 12-1 and are presented in Table 12.3. Corresponding
reaction rate coefficients have been estimated based on anion deceleration to \(|q|\Delta V_{\text{ISAS}}\) (q is the anion charge) for the respective curves. Points from the two attenuation curves for ZrF\(_3^-\) between 0 and 1.1 mTorr were plotted together and a linear regression was applied. The slope from this curve was used to calculate the attenuation cross section and an average of the two \(\Delta V_{\text{ISAS}}\) was used for the rate coefficient calculation.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Initial Ion Kinetic Energy Estimate [eV](^b)</th>
<th>Pressure Range [mTorr]</th>
<th>Number of Points(^c)</th>
<th>Figure</th>
<th>Cross Section ([x 10^{-15} \text{ cm}^2])</th>
<th>Rate Coefficient ([x 10^{-9} \frac{\text{ cm}^3}{\text{ molecule} \cdot \text{s}}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{89}\text{YF}_3^-)</td>
<td>5.3</td>
<td>0 – 2.5</td>
<td>8</td>
<td>10–10</td>
<td>7.6</td>
<td>2</td>
</tr>
<tr>
<td>(^{90}\text{ZrF}_3^-)</td>
<td>5(^a)</td>
<td>0 – 1.1</td>
<td>6(^a)</td>
<td></td>
<td>19</td>
<td>5</td>
</tr>
</tbody>
</table>

Curves used for cross section calculations are shown in Figure 12-1. The corresponding pressure ranges and number of data points are given in the third and fourth columns respectively. A brief description of the calculations follows, more details can be found in section 10.5 where concepts and methods were introduced. Cross sections were calculated using Eq 10.3 and 10.4 because the data plotted linearly on a log\(_{10}\) plot as for first order reactions. Column 2 represents a lower limit estimate for the ion kinetic energy based on \(K_0 = |q|\Delta V_{\text{ISAS}}\) where q is the ion charge and \(\Delta V_{\text{ISAS}}\) is the ion source – ISA deck voltage offset given by Eq 7.1. These values were used to estimate reaction rate coefficients based on the measured cross sections.

a) The first three points of the two attenuation curves for ZrF\(_3^-\) attenuation in NO\(_2\) were plotted together. A linear regression was applied and the slope used to calculate the attenuation cross section. The value in column two is an average of the two \(\Delta V_{\text{ISAS}}\) used.

### 12.5 Discussion

Transmission of SrF\(_3^-\) in NO\(_2\) with the current system was observed to be greater than 95% over a range of 7 mTorr NO\(_2\) pressure under the experimental conditions used for the data in Figure 12-1. Conversely, large attenuation cross sections of 7.6 \(x 10^{-15}\) and 1.9 \(x 10^{-14}\) cm\(^2\) respectively were observed for YF\(_3^-\) and ZrF\(_3^-\) in NO\(_2\) respectively, with associated isobar suppression factors of YF\(_3^-\)/SrF\(_3^-\) = 5 \(x 10^{-5}\) and ZrF\(_3^-\)/SrF\(_3^-\) = 4 \(x 10^{-6}\) at 6 mTorr cell pressure. Combined with the relative anion production efficiencies discussed in the introduction of this chapter, use of matrix assisted sputtering and the ISA has the potential for relative isobar
suppressions of $\text{YF}_3^-/\text{SrF}_3^- = 10^{-9}$ and $\text{ZrF}_3^-/\text{SrF}_3^- = 10^{-10}$, and $\text{YF}_3^-/\text{SrF}_3^- = 10^{-15}$ and $\text{ZrF}_3^-/\text{SrF}_3^- = 10^{-16}$ with sample preparation to lower impurities to ppm levels.

Despite the large cross sections, both $\text{YF}_3^-$ and $\text{ZrF}_3^-$ attenuations plateaued, as is generally observed with large attenuations. Possible causes have been explored most extensively in the case of $\text{S}^- + \text{NO}_2$ (see sections 10.3.5.1, and 10.3.5.2) and there is likely more than one mechanism at work.

Electron and O transfer were the major reaction channels observed for both $\text{YF}_3^-$ and $\text{ZrF}_3^-$ in NO$_2$, accounting for 10 – 20% of the anion losses each. With the limited data available, the O capture cross section appears to be similar to the electron transfer cross section $\text{ZrF}_3^-$ although the electron transfer seems to account for twice the $\text{ZrF}_3^-$ losses. Reactions with O$_2$ may explain the relatively large observed $\text{ZrF}_3^-$ attenuation in air. On the other hand, both electron transfer and O transfer appeared to account for the same amount of $\text{YF}_3^-$ loss. Based on the apparent exothermicity of the reactions, the bond dissociation energies $D(\text{O – ZrF}_3^-)$ and $D(\text{O – YF}_3^-)$ are likely greater than $D(\text{O – NO})$, and the electron affinities of ZrF$_3$ and YF$_3$ are likely less than that of NO$_2$.

For molecular anion production with up to 8 fluorine atoms, $\text{YF}_4^-$ represents almost 100% and $\text{ZrF}_5^-$ represents $> 98\%$ of the respective fluorine anions produced during sputtering with target matrices as described in Table 12.1. Then, O capture may be very electronically favorable. The observed $\text{YF}_3^-$ and $\text{ZrF}_3^-$ reactivities for O transfer from NO$_2$ may be even greater for a more weakly bound oxide that does not have the barriers observed with N$_2$O (section 10.3.3), such as O$_3$ (Table 9.1). Furthermore, the anion is always incident on an O atom with O$_3$ as opposed to NO$_2$. Reactions with a gas that redily loses an F atom, such as BF$_3$, may also lead to larger attenuations.

The relatively high level of the NO$_2$ compound observed in Figure 12-3 (several percent of the initial $\text{YF}_3^-$ current), $(\text{YF}_3\cdot\text{NO}_2)^-$, can also be understood if one considers the NO$_2$ molecule as filling the role of the fourth F atom of a $\text{YF}_4^-$ anion. Anusiewicz (2009) has modelled such structures theoretically, showing that NO$_2$-ligand molecules can have very large vertical electron detachment thresholds and form even stronger anions than F-ligand molecules.
13 Summary and Conclusions

This thesis has been an attempt to summarize basic concepts for and early endeavours at harmonizing low energy gas-phase reactions using rf quadrupole collision cell technology for enhanced accelerator mass spectrometry capabilities, a technique that may be called RFQ–AMS. Experiments were conducted using a prototype, single collision cell rf quadrupole instrument, named Isobar Seperator for Anions (ISA) currently, coupled to a 2 MV AMS system located downstream for ion analysis (chapter 7).

Two major applications have been outlined: gas-phase reactive isobar suppression with ion beams for rare to abundant isotope ratio measurements, and gas-phase anion reaction studies largely free from product identification ambiguities. In chapter 2, ‘rare to abundant ratio’ was loosely given as < 10^{-12} for typical analyses. Although several instruments (see section 2.2) have large enough mass resolution (m/Δm > 10^5) to separate many atomic isobars (see Appendix D), absolute count rates > 500 c/s are required and dynamic ranges are typically limited to ≤ 10^4 (see table 2.2). Conversely, dynamic ranges > 10^{14} and count rates on the order of counts per day are established domains for many analyses with AMS systems. Coupled with the variety of anions readily produced in AMS Cs^+ sputter sources, RFQ–AMS presents interesting opportunities for gas–phase chemistry research.

13.1 Isobar Suppression

A major goal of this project was to increase the analytical trace to abundant isotope ratio measurement capabilities of smaller AMS systems by suppressing isobars using gas-phase reactions before the accelerator. As an isobar filter, the ISA shows great promise and NO_2 has been found to be a very efficient gas with several eV kinetic energy ion beams when the analyte has larger electron affinity than NO_2 and the unwanted isobar does not, such as ^36Cl and ^36S. In cases where the elemental electron affinity is relatively weak, such as for Sr, matrix assisted sputtering can be used for production of molecular anions with very large electron affinity, such as SrF_3^– (chapter 12). Care should be taken, however, to ensure that unwanted reaction channels are not available because of excessive kinetic energy during injection into the collision cell. Consideration of electron affinity, mass and kinetic energy together is important if losses (eg from electron detachment) are to be avoided, as illustrated in Figure 6-2 and Figure 9-5.
13.1.1 Application to $^{36}$Cl

The prototype has already proven very successful for suppression of the $^{36}$S$^-$ and $^{12}$C$_3^-$ isobars for $^{36}$Cl$^-$ analyses using NO$_2$ gas with deceleration from 20 keV to $\leq$ 12 eV and no moderation of the ion beam energy spread (discussed in section 10.3.6) with a cooling cell or electric analyzer. With 6 – 8 mTorr NO$_2$ in the ISA collision cell, attenuations of $10^{-7}$ for S$^-$ and $10^{-8}$ for C$_3^-$ were observed with associated attenuation cross sections of $6.6 \times 10^{-15}$ cm$^2$ and $4.2 \times 10^{-15}$ cm$^2$ respectively, while only 70% attenuation was observed for Cl$^-$. Stripping to $q = +3$ at an accelerator terminal voltage of $V_T = 1.75$ MV led to further C$_3^-$ suppression. Only the $^{12}$C$_3^- \rightarrow 3(^{12}$C$^+)$ coincidence break-up signal added to the $^{36}$Cl$^{+3}$ blank and the peaks were separated because of different total energy loss during passage through the ionization detector ‘window’ (section 10.4 and Figure 11-1). Under the experimental conditions described and with some sample preparation to reduce impurities to parts per million, present limits were calculated to be $^{36}$S$^-$/Cl$^- \sim 4 \times 10^{-16}$ and $^{12}$C$_3^-$$/Cl^- \sim 1.2 \times 10^{-16}$ in section 10.6.

Scalability over at least 2 orders of magnitude was also demonstrated under the above conditions (stripping to $q = +3$ using $V_T = 1.75$ MV). Four $^{36}$Cl reference standards covering the range $4 \times 10^{-13} \leq ^{36}$Cl/Cl $\leq 4 \times 10^{-11}$ were analyzed (section 11.2), and the measured $^{36}$Cl/Cl ratios plotted very well linearly against the accepted values (Figure 11-2). A sample impurity content S/Cl $\leq 6 \times 10^{-5}$ was measured and a background level of $^{36}$S$^-$/Cl $\leq 9 \times 10^{-15}$ was determined.

Attenuation curves for Cl$^-$ and S$^- +$ NO$_2$ with $V_T = 1$ MV for stripping to $q = +1$ were the same as those taken using $V_T = 1.75$ MV for stripping to $q = +3$, suggesting that $^{36}$Cl$^-$ analyses at lower voltages may also be possible. However, full background analyses similar to those in chapter 11 have not been completed up to present. For example, contributions to the blank from molecular anions such as $^{12}$C$_3^-$ and $^{18}$O$_2^-$ must be determined and may require higher pressures in the stripping canal for molecular destruction.

Nonetheless, this technique is already proving very powerful. For comparison, Berkovits et al. (1989) measured $\sim 10^3$ S$^-$ attenuation with no appreciable Cl$^-$ losses for 100 keV kinetic energy ion beams interacting with $\lambda = 532$ nm (2.33 eV) photons at a density of $> 10^{17}$ photons/cm$^2$ over a 1.2 m interaction region. Such photon energy is very close to the NO$_2$ electron affinity, 2.273 eV, but ion–photon interaction cross sections under these conditions (non-relativistic ion kinetic energy, non-resonant photon interactions) are generally on the order of $10^{-17}$ cm$^2$. The measured S$^-$ attenuation cross section was $1.0 \pm 0.2 \times 10^{-17}$ cm$^2$ (discussion can
also be found in section 2.5), more than 2 orders of magnitude below the $S^-$ attenuation cross section in NO$_2$ measured with the ISA.

Similarly, using an rf quadrupole cooling cell to facilitate ion-photon interactions for non-resonant laser induced electron dissociation, the group at Oak Ridge has so far achieved an $S^-/Cl^-$ relative suppression of $3 \times 10^{-4}$ (Galindo-Ulibarri et al. 2008, Liu et al. 2005). Ions were injected into the cooling cell with 40 eV kinetic energy for interaction with $\lambda = 1064$ nm photons from a continuous wave Nd:YAG laser, and Cl$^-$ transmission was about 50%. More details can be found in sections 2.5 and 6.3.1.

Knie et al. (1997) approached the $^{36}S^- - ^{36}Cl^-$ isobar issue by attempting to effectively increase the resolution of the isobar signal peaks in the final detector. Gas was leaked into a 135° magnet after the accelerator in order to narrow signal peak widths and gain in the peak-to-peak separation between isobars, using an accelerator terminal voltage of $V_T = 13.5$ MV for stripping to $q = +9$. The ionization chamber also had 5 separate $\Delta E$ measurement stages with additional trajectory horizontal position and horizontal and vertical angle measurement capabilities in order to reject signals from scattered ions entering the detector with analyte ions. With 9 mTorr N$_2$ gas (found to be better than H$_2$, He, Ar, CH$_4$ and C$_6$H$_{10}$) in the magnet, the $S^-$ signal corresponding to blank was reduced by a factor of 300.

### 13.1.2 Application to Sr and Cs

Matrix assisted sputtering, by saturating the target material with PbF$_2$ powder, was used to both boost the Sr available for AMS detection by creating SrF$_3^-$ in the ion source, and suppress the isobars Y and Zr as they preferentially form YF$_4^-$ and ZrF$_5^-$ respectively (see chapter 12). Further attenuation was achieved using the ISA with NO$_2$ and deceleration to 4.8 eV ion kinetic energy.

Transmission through the ISA at base pressure (no gas in the collision cell) was $\sim 90\%$ for SrF$_3^-$, and there was no significant attenuation with up to 7 mTorr NO$_2$ gas in the cell (Figure 12-1). Conversely, large attenuation cross sections of $7.6 \times 10^{-15}$ cm$^2$ and $1.9 \times 10^{-14}$ cm$^2$ were observed for YF$_3^-$ and ZrF$_3^-$ respectively in NO$_2$, with associated isobar suppression factors of $YF_3^-/SrF_3^- = 5 \times 10^{-5}$ and $ZrF_3^-/SrF_3^- = 4 \times 10^{-6}$ at 6 mTorr cell pressure. Combined with the relative anion production efficiencies, use of matrix assisted sputtering and the ISA has the potential for relative isobar suppressions of $YF_3^-/SrF_3^- = 10^{-9}$ and $ZrF_3^-/SrF_3^- = 10^{-10}$ (calculated in section 12.5). Detection limits for $^{90}Sr/Sr < 10^{-16}$ could then be achieved with sample
preparation to reduce contaminants to ppm levels, considering the relative scarcity of $^{90}$Y (although it is a daughter product of $^{90}$Sr).

A note here is made about the possibility of $^{135,137}$Cs analysis using CsF$_2^-$ . Data was not included in this thesis but more details may be found in Eliades et al. (2011). Attenuation of BaF$_2^-$ was found to be > 5 orders of magnitude in the ISA with NO$_2$ gas and deceleration to 4.8 eV, while CsF$_2^-$ had transmission > 10%, and a relative attenuation of BaF$_2^-$/CsF$_2^-$ = 2 x 10$^{-5}$ was measured. The BaF$_2^-$ attenuation cross section in NO$_2$ was the largest measured using the ISA, 6.8 x 10$^{-14}$ cm$^2$. Relative matrix assisted sputtering efficiencies give BaF$_2^-$/CsF$_2^-$ ~ 5 x 10$^{-4}$ so that an isobar suppression of BaF$_2^-$/CsF$_2^-$ = 10$^{-8}$ has effectively been achieved using the two techniques.

As a comparison, Tumey et al. (2008, 2009) have attempted to assess $^{90}$Sr analytical capabilities using traditional AMS with an accelerator terminal voltage $V_T$ > 8 MV, but with a modified detector for increased $^{90}$Zr discrimination. They also found that Zr contamination was coming from standard target holders made of Al, and use of high purity Ni holders instead led to a suppression of the Zr signal by a factor of 10 (Tumey et al. 2008). Using $V_T$ = 9.25 MV for stripping to q = +11, they reported a detection blank of $^{90}$Sr/Sr = 5.98 x 10$^{-13}$ (Tumey et al. 2009).

As with the measurements reported in this thesis, SrF$_3^-$ was used, but not with matrix assisted sputtering. The target matrix was SrF$_2$ only so that the matrix was already F deficient for sputtering to SrF$_3^-$ . Furthermore, it was found that the SrF$_3^-$ current from the high purity Ni target holder was double that from the Al target holder (Tumey et al. 2008). Experience at IsoTrace Laboratory has indicated that Al is very reactive with F during 4 keV Cs$^+$ sputtering and produces large currents of AlF$_4^-$, the main sputter product in a PbF$_2$ rich matrix. On the other hand, the main sputter product with Ni is NiF$_3^-$ and anion currents are weaker. The difference in SrF$_3^-$ observed by Tumey et al. (2008) is likely rooted in the competition between sputter target holder and target matrix constituents for F reaction. Mixing a sufficient amount of PbF$_2$ powder with the target material should boost SrF$_3^-$ and decrease the relative signal from ZrF$_3^-$.

### 13.2 Gas–Phase Anion Reaction Studies

Several anion–gas reactions were studied in chapters 10 and 12, and these only represent a portion of the work that was carried out over the tenure of these PhD studies. Emphasis was placed on those reactions relevant to isotopes of interest for AMS trace abundance ratio measurements.
In the case of $S^- + NO_2$, a dynamic range of $10^9$ was demonstrated (Figure 10-10) and there was no sign that this represented the upper limit. Furthermore, analysis of the fragments after break-up in the tandem accelerator stripping canal allowed for relatively unambiguous identification of reaction products. With larger accelerators there is also potential for further resolution by using dE/dx techniques for elemental identification based on differences in nuclear properties.

Perhaps more interesting from a physical chemistry perspective, reactions between NO$_2$ and YF$_3^-$ and ZrF$_3^-$ were also reported (chapter 12). Because of the relative anion production efficiencies during Cs$^+$ sputtering, the SrF$_3$ electron affinity is predicted to be very large while those of YF$_3$ and ZrF$_3$ are predicted to be small. This was supported by work with the ISA with deceleration to 4.8 eV and NO$_2$ gas showing that electron transfer was a major reaction channel for YF$_3^-$ and ZrF$_3^-$ loss, suggesting the respective electron affinities are less than 2.273 eV, while SrF$_3^-$ had > 90% transmission.

Oxygen transfer was also found to have comparable efficiency to electron transfer for YF$_3^-$ and ZrF$_3^-$ losses with NO$_2$, likely because the resulting fluoro-oxide molecular anions were analogous to the super anion equivalents ZrF$_5^-$ and YF$_4^-$. This is somewhat surprising given the expected ranges for electron versus atom tunnelling. Furthermore, in other cases where O transfer is exothermic to first order (such as with Si$^-$ and Al$^-$ + NO$_2$, not reported in the thesis), electron transfer was still found to dominate. A comparison with O$_3$, which has slightly weaker electron affinity than NO$_2$ but a much weaker O-bond dissociation energy, may be interesting (a summary of properties may be found in section 9.1). Unlike NO$_2$, an ion is always incident on an O atom with O$_3$ and there should not be the same quantum barriers as associated with N$_2$O (see section 10.3.3).

Also of interest was the observation of YF$_3^-(NO_2)$ at levels of several percent of the initial YF$_3^-$ ion current. The addition of the NO$_2$ molecule may be analogous to the addition of an O or F atom, and may represent another form of the super-anion structure. Anusiewicz (2009) has reported analogous –NO$_2$ superhalogen structures.

That said, the main anion reaction channel has been electron transfer with NO$_2$ when the atomic or molecular electron affinity was less than that of NO$_2$ in all other cases studied, including Al$^-$, Si$^-$, O$^-$ and C$^-$ not reported in this thesis. However, all major attenuations showed a plateau at some level. While plateau levels and onset pressures varied for different anions, they were consistent for a given anion over the limited range of ISA decelerations used.
Given that attenuation measurements ranged over several mTorr and that at least 2 collisions can be expected on average by 1 mTorr under the experimental conditions employed, it seems unlikely that the plateaus were merely due to NO2 impurities or N2O4 levels. Some possibilities have been addressed, for example in section 10.3.5, and more than one mechanism is likely responsible in many or all cases. At this point, however, the true nature remains unclear. From an isobar attenuation standpoint, more study is merited as lowering attenuation plateau levels should ultimately lead to better sensitivity limits.

As a final note, many of the results obtained over the course of this work would have been much more ambiguous or completely confounding without the reaction product identification available because of the AMS system (eg see section 10.3.2, Figure 10-11 and Figure 11-1). In several cases, isotopes were used to confirm results where atomic anion ambiguities arose (resolution by dE/dx was not available with the AMS system used).

13.3 Future Development

Deceleration of keV ion beams to eV energies for injection into the ISA still represents a hurdle in the process. During electrostatic deceleration, the divergence of an ion beam increases and, in effect, a portion of the axial kinetic energy is transferred to the radial direction, placing larger demands on the rf trapping potential and increasing the energy during collisions with gas. Trajectory amplitudes are also larger which affects transmission through apertures. These issues were addressed in chapters 4 and 5. Furthremore, space charge should be considered for large-current anion beams.

Increasing the rf voltage and frequency can compensate, but leads to greater rf heating (Eq 4.42). Even with constant quadrupole q2 value, a q2 attained using larger voltages and frequencies will lead to larger rf heating than the same q2 attained using lower voltages and frequencies. Conversely, the same q2 attained using lower voltage and frequency leads to larger trajectory amplitudes than that attained using larger voltage and frequency. Although the current ISA deceleration stage has proven useful for the initial studies contained in this thesis, better design that minimized beam divergence would improve performance.

Phenomena such as ‘q2 focusing’ and low kinetic energy transmission losses at apertures have been demonstrated for uncooled ion beams in the ISA in chapter 8, and the majority of ions in the ion beams used were calculated to have large radial kinetic energy (> 0.5 eV) on average. There are several approaches to improving transmission in such circumstances.
In one approach, the ion beam could be directly injected into a collision cell (for cooling, reaction or both) directly from the deceleration stage. Results from the Oak Ridge device (section 6.3.1), however, suggest limitations to this approach. First, ions must typically be above 30 eV axial kinetic energy when decelerated from tens of keV in order to maintain a reasonable beam divergence after electrostatic deceleration. For smaller molecules and atomic anions this can result in significant losses to electron detachment during initial collisions with gases such as Ar and NO₂. Second, differential pumping between the deceleration region and collision cell high pressure region is difficult, leading to losses from high kinetic energy collisions before full deceleration from keV energies. Even using He as a cooling gas, the Oak Ridge cooler has not attained greater than 51% transmission for Cl− under the required experimental conditions.

Another approach, the design currently used in the ISA, is to have an rf quadrupole ion guide differential pumping region between the deceleration stage and collision cell. This section could be modified. With wider entrance apertures on the collision cell, there could be higher transmission of ions with larger radial kinetic energy. It was found that (section 8.1.3) 100% transmission from the drift region into the collision cell through φ3 mm apertures could be attained for > 100 nA ion beams while ions were decelerated to < 10 eV axial kinetic energy (with cell exit apertures removed). However, this required application of > 100 V to the apertures. Subsequent cooling within the cell should confine the ion beam close to the axis and reduce the radial energy. In this case, there would be an advantage to using a longer collision cell since lower pressures could be used while maintaining the same average number of collisions and maintaining good differential pumping.

For gas-phase anion reaction studies using rf quadrupole accelerator mass spectrometry, RFQ–AMS–GPAR, better control of the ion beam kinetic energy spread and knowledge of the excited state distribution is needed. Sputter sources used in AMS readily produce a very wide variety of exotic anions in appreciable currents, but there can be very large excited state populations and ion beam kinetic energy spreads. An electric analyzer with ΔK/K = 2.5 x 10⁻³ (K is kinetic energy) would restrict a 20 keV ion beam to within 50 eV. A cooling cell following the ISA deceleration stage would then facilitate reduction of the kinetic energy spread and de-excitation of the excited states.

Criteria for the selection of cooling gases include reactivity, mass, pumping, impurities and physical geometry, as discussed in sections 6.4, 9.2 and 10.6. In four of these regards, CH₄ presents some interesting advantages over the traditionally used He and Ar cooling gases.
(enumerated in section 10.6), although there may be more impurities and reactivity may be an issue for some anions. In the end, experiment will dictate which gas should be used.

An attenuation plateau has been observed for all major attenuations observed in NO₂, the nature of which remains unresolved. This was examined in the context of the S⁻ + NO₂ plateau with onset near 6 mTorr cell pressure (in the prototype ISA) at 10⁻⁷ of the original S⁻ signal. There may be contributions from systematic phenomena such as anion neutralization at high kinetic energy in the region before the ISA from collisions with residual gas, and subsequent re-ionization after the ISA from interactions with residual gas. Other sources may be reaction based as equilibrium conditions are reached at higher pressures. This could point to some advantages in maintaining a minimum kinetic energy above thermal or alternating the axial kinetic energy as the ion traverses the cell. Suitable gradient bars or segmented rf quadrupole rods could be used.

While a cooling cell may be advantageous for RFQ–AMS–GPAR, isobar suppression applications are less demanding. All that is required is large analyte transmission and large isobar suppression. Anions for the less massive elements, such as Cl⁻, showed significant (on the order of 70%) losses when directly injected into NO₂, and in such cases an initial cooler (eg using CH₄ or He) should help increase transmission. However, transmission approached 100% when the anion mass and electron affinity were larger than NO₂, as was the case for SrF₃⁻ (section 12.1). For many isobar suppression applications, a single cell for cooling and reacting will likely be sufficient. Similar considerations to those outlined above suggest a longer cell with large entrance aperture.

### 13.4 Concluding Remarks

In the end, low energy gas-phase reaction based isobar suppression using rf quadrupole instruments is proving to be a very powerful technique, as predicted by Douglas (1989) so many years ago (see section 3.1). The prototype, single collision cell ISA has already demonstrated ³⁶Cl/Cl = 4 x 10⁻¹³ measurement capabilities with AMS using an accelerator terminal voltage of 1.75 MV, and there was indication that ≤ 1 MV may also be sufficient for such analyses (section 10.3.5.1). Additionally, there is indication that analysis of isotopes such as ⁹⁰Sr and ¹³⁵,¹³⁷Cs, previously largely inaccessible to AMS, can be routinely measured using a combination of matrix assisted sputtering, isobar suppression in an ISA and analysis by AMS.

Combining rf quadrupole technology with an AMS system has also shown great promise for applications in physical chemistry, especially for anions that are not readily produced in most
of the commonly used ion sources in other disciplines of mass spectrometry. A dynamic range ~ $10^9$ has been demonstrated and reactions between NO$_2$ and the relatively exotic anions YF$_3^-$ and ZrF$_3^-$ have been studied. Furthermore, examples were presented of fragment identification after stripping in a tandem accelerator that can be used to determine or infer the atomic constituents of reaction products for relatively unambiguous identification.

An end in one sense is a beginning in another, and the end of this thesis should mark the beginning of a prosperous future for what may tentatively be called RFQ–AMS.
References


Dunkin D.B., Fehsenfeld F.C. and Ferguson E.E. (1972) Thermal energy rate constants for the reactions NO2⁻ + Cl₂ → Cl⁻ + NO2, Cl⁻ + NO2 → Cl⁻ + NO2Cl, SH⁻ + NO2 → NO2⁻ + SH, SH⁻ + Cl₂ → Cl⁻ + SH, and S⁻ + NO2 → NO2⁻ + S. *Chemical Physics Letters*, 15, 257-259.


Eliades J. (2006) Contaminant ion beams from a Cs⁺ gun – New sources of contamination in AMS. *MSc Thesis, IsoTrace Laboratory*, University of Toronto (soon to be located at CANAMS, University of Ottawa).


distribution of Be, C, Cl and Al ions at the Lund Pelletron accelerator with the recently modified terminal
Kilius L.R., Baba N., Garwan M.A., Litherland A.E., Nadeau M.-J., Rucklidge J.C., Wilson G.C. and Zhao
Toronto, 250 pp.
King F.L. and Harrison W.W. (1989) Collision induced dissociation of polyatomic ions in glow discharge mass
Klepper O. (1997) Bound-state beta decay and nuclear lifetime measurements at the storage-cooler ring ESR.
Nuclear Physics A626, p. 199c – 213c.
Knie K., Faestermann T. and Korschinek G. (1997) AMS at the Munich gas-filled analyzing magnet system
Great Britain, 441 pp.
spectrometry: development, status and applications. Journal of Analytical Atomic Spectrometry, 19, p. 561
– 570.
the analysis of platinum group elements at low levels in insulating materials. Nuclear Instruments and
Kummerlöwe G. and Beyer M.K. (2005) Rate estimates for collisions of ionic clusters with neutral reactant
molecules. International Journal of Mass Spectrometry, 244, p. 84 – 90.
Nuclear and Particle Science, 40, p. 411 – 438.
Langevin M.P. (1905) Une formule fondamentale de théorie cinétique. Annales de Chimie et de Physique, sér.
8, tome 5, p. 245 – 288.
nitration of first-, second-, and third-row atomic cations in reactions with nitrous oxide: periodicities in
University of Toronto, 152 pp.


Software References

MATLAB 7.0, version 7.0.0.19920 (R14), Mathworks Inc., Matick, Massachusetts, U.S.A. [on page 5—38, 9–142]

Origin 7.5 SR7 V7.5886 (B886), © 1991 – 2008, OriginLab Corporation, Northhampton, Massachusetts, U.S.A
**APPENDIX A**

*Constants, Units and Conversions*

A reference of fundamental constants, unit conversions and formulae expressed in non-SI units commonly used throughout the thesis.

**A.I Summary (‘Cheat-Sheets’)**

<table>
<thead>
<tr>
<th><strong>Table A 1: Fundamental Constants</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Avogadro constant</strong></td>
</tr>
<tr>
<td><strong>Boltzmann constant</strong></td>
</tr>
<tr>
<td><strong>electron rest mass</strong></td>
</tr>
<tr>
<td><strong>elementary charge</strong></td>
</tr>
<tr>
<td><strong>gravity, standard acceleration of</strong></td>
</tr>
<tr>
<td><strong>neutron rest mass</strong></td>
</tr>
<tr>
<td><strong>gas constant, universal molar</strong></td>
</tr>
<tr>
<td><strong>Planck constant</strong></td>
</tr>
<tr>
<td><strong>proton rest mass</strong></td>
</tr>
<tr>
<td><strong>speed of light in vacuum</strong></td>
</tr>
</tbody>
</table>

\[ *n \rightarrow \frac{1}{2} H + \beta^- + \bar{\nu} \] with $Q = 0.782354 \text{MeV}$ and $\tau_{1/2} = 614.8 \text{s}$ (Firestone and Shirley 1996, p. 1)

Table A 2: Pressure Conversions

\[ 1 \cdot \text{atm} = 760 \cdot \text{mmHg} = 760 \cdot \text{Torr} = 101.325 \cdot \text{kPa} = 1.01325 \cdot \text{bar} \]

\[ N = \frac{P}{k_B T} \]

N = \frac{P}{k_B T} \quad \text{From ideal gas law: number of atoms or molecules per unit volume}

\[ N = N_T/V \quad \text{pressure P, temperature T, Boltzmann constant } k_B \]

Table A 3: Mass Conversions

\[ 1 \cdot \text{amu} \equiv \frac{10^{-3}}{N_A} \text{kg} \]

\[ 1 \text{kg} = 6.022 \times 10^{26} \quad 5.610 \times 10^{29} \quad 1.098 \times 10^{30} \]

\[ 1 \text{ amu} = 1.661 \times 10^{-27} \quad 1 \quad 931.494 \quad 5.486 \times 10^{-4} \]

\[ 1 \text{ MeV/c}^2 = 1.783 \times 10^{-30} \quad 1.074 \times 10^{-3} \quad 1 \quad 1.9569514 \]

\[ 1 \text{ m_e} = 9.109 \times 10^{-31} \quad 1822.8885 \quad 0.510998910 \quad 1 \]

Often \(1/c^2\) is set equal to unity so that mass is expressed in pure energy units, MeV.

Table A 4: Energy Conversions

<table>
<thead>
<tr>
<th>Joule</th>
<th>calorie</th>
<th>electron volt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 J</td>
<td>1</td>
<td>6.2415 x 10^{18}</td>
</tr>
<tr>
<td>1 cal</td>
<td>4.1868</td>
<td>1</td>
</tr>
<tr>
<td>1 eV</td>
<td>1.6022 x 10^{-19}</td>
<td>3.8267 x 10^{-20}</td>
</tr>
<tr>
<td>1 kJ/mol</td>
<td>10^{3}/N_A \sim 1.66 \times 10^{-21}</td>
<td>0.2388 \times 10^{3}/N_A</td>
</tr>
<tr>
<td>1 kcal/mol</td>
<td>6.9523 \times 10^{-21}</td>
<td>10^{3}/N_A \sim 1.66 \times 10^{-21}</td>
</tr>
</tbody>
</table>


Table A 5: Temperature and Non-Relativistic Kinetic Energy in Non-SI units

\[ T[K] = \frac{E}{k_B} \approx 11505 \cdot E[eV], \quad 20^\circ C = 293 K \approx 0.025 eV \]

\[ \sqrt{\frac{2KE}{m}} = \sqrt{\frac{2 \times 10^7 N_A \cdot e}{m[amu]}} \approx 1.39 \times 10^6 \sqrt{\frac{KE[eV]}{m[amu]}} \]

\[ v \cdot \left[ \frac{m_e}{c} \right] = \sqrt{\frac{T[K]}{m[amu]}} \approx 12895 \sqrt{\frac{T[K]}{m[amu]}} \]

Temperature (T) and energy (E)

Non-relativistic kinetic energy (KE), mass (m) and speed (v)

Temperature (T), non-relativistic mass (m) and speed (v)
A.II  Pressure Conversions

A column of liquid Hg at standard temperature and pressure (STP) rises 760 mm, defining the units millimetre mercury (mmHg) and atmosphere (atm):

\[ 760 \text{mmHg} \equiv 1 \text{atm} \]

In honour of Evangelista Torricelli who made the first Hg barometer in 1644 (or his student in 1643) which was also used as the first Hg vacuum pump, a unit Torr was named:

\[ 1 \text{mmHg} \equiv 1 \text{Torr} \]

The density of mercury at STP is discussed in Bettin and Fehlauer (2004), given as \( \rho_{\text{Hg}}(20^\circ \text{C}) = 13546 \ \text{kg m}^{-3} \), and the correction factor

\[ \frac{-\partial \rho}{\partial T} = (1.812 \pm 0.005) \times 10^{-4} \ K^{-1} \]

is given on p. S20 so that \( \rho_{\text{Hg}}(0^\circ \text{C}) = 13595 \ \text{kg m}^{-3} \). Let \( P \) be pressure, \( F \) be force, and \( A \) be the cross-sectional area of a column of height \( h \) and volume \( V \) of Hg:

\[
P = \frac{F}{A} = \frac{\rho_{\text{Hg}} V \cdot g}{A} = \frac{\rho_{\text{Hg}} (h \cdot A) \cdot g}{A} = \rho_{\text{Hg}} h \cdot g
\]

\[
\therefore 1 \text{Torr} \equiv 1 \text{mmHg} = 13595 \frac{\text{kg}}{\text{m}^3} \cdot 10^{-3} \text{m} \cdot 9.80665 \frac{\text{m}}{\text{s}^2} = 133.3224 \left[ \frac{\text{kg} \cdot \text{m}}{\text{s}^2} \cdot \frac{1}{\text{m}^2} = \text{Pa} \right]
\]

The Pascal, (Pa), is the current SI unit of pressure. Finally,

\[ 1 \text{bar} \equiv 10^{5} \text{Pa} \equiv 100 \text{kPa} \]

\[ 1 \text{atm} \equiv 101325 \text{Pa} \equiv 1.01325 \text{bar} \]

The ideal gas law with pressure \( P \), volume \( V \), number of moles of gas \( n \), total number of gas atoms or molecules \( N_T = n \times N_A \), temperature \( T \) and with constants \( R \), \( K_B \), and \( N_A \) given above,

\[
P[\text{Pa}] \cdot V[\text{m}^3] = n[\text{mole}] \cdot R_G \cdot \left[ \frac{J}{\text{mol} \cdot K} \right] \cdot T[K] = N_T[\#] \cdot k_B \left[ \frac{J}{K} \right] \cdot T[K]
\]

The last form is slightly more intuitive as it relates pressure and volume to the number of molecules and energy, \( k_B T \). With \( N = N_T/V \) representing the number of atoms or molecules per unit volume,

\[
N = \frac{N_T}{V} = \frac{P}{k_B T} \left[ \frac{101325 \text{Pa} \cdot \text{m}^3}{760 \text{Torr} \cdot 10^6 \text{cm}^3} \right]
\]

\[
\Rightarrow N[\frac{\#}{\text{cm}^3}] = 1.3332237 \times 10^{-4} \left( \frac{P[\text{Torr}]}{(k_B T)[J]} \right)
\]
A.III Mass Conversions

\[ M_{\text{mol}} = \text{the mass of 1 mole of } ^{12}\text{C} \equiv 12 \text{g} \quad ; \quad \text{The mass of one } ^{12}\text{C atom} \equiv 12 \text{amu} \]

\[ \therefore 1 \text{g} \equiv \frac{M_{\text{mol}}}{12} \equiv \frac{1 \text{mol} \cdot N_A \text{units/ mol} \cdot 12 \text{amu/ unit}}{12} = N_A \text{amu} \]

\[ \therefore \text{amu} \equiv \frac{10^{-3}}{N_A} \text{kg} \approx 1.66 \times 10^{-27} \text{kg} \]

\[ E[J] = m[\text{kg}] \cdot c^2 \left[ \frac{\text{g}}{c^2} \right]^2 \]

\[ \Rightarrow m[\text{kg}] = \frac{E[J]}{c^2 \left[ \frac{\text{g}}{c^2} \right]^2} = \frac{(2.99792 \times 10^8 \text{ m/s})^2}{c^2} \cdot \frac{E \left[ \text{Mega-} \right]}{10^6 \frac{eV}{1.602 \times 10^{-19} J}} \]

\[ \therefore \text{kg} = \frac{10^{-6} c^2}{e} = 5.609589 \times 10^{29} \frac{MeV}{c^2} \]

\[ \therefore \text{amu} = \frac{10^{-3} c^2}{e \cdot N_A} \frac{MeV}{c^2} = 931.49403 \frac{MeV}{c^2} \]

Often the term \( \frac{1}{c^2} \) is set equal to 1 so that mass is measured in pure energy units.

A.IV Energy Conversions

\[ eV = \frac{eJ}{C} = \frac{1.602 \times 10^{-19} C}{e} \cdot \frac{eJ}{C} = 1.602 \times 10^{-19} J \]

\[ 1 \text{ cal} = 4.1868 J \]

\[ \therefore 1 \frac{kcal}{mol} = 4.1868 \frac{kJ}{mol} \]

\[ \therefore 1 \frac{kJ}{mol} = 10^3 J \cdot \frac{eV}{1.602 \times 10^{-19} J} \cdot \frac{mol}{6.022 \times 10^{23} \text{ units}} \cdot \frac{1}{mol} = 0.010364269 eV \]

\[ \therefore 1 \frac{kcal}{mol} = 4.1868 \cdot 0.010364269 eV = 0.043393 eV \]

\[ T = \frac{E[J]}{k_B [J/K]} = 1.602 \times 10^{-19} J \cdot \frac{eV}{1.38 \times 10^{-23} J/K} \]

\[ \Rightarrow T[K] \approx 11505 \cdot E[eV] \text{ and } 20^0C = 293K \approx 0.025 eV \]
A.V Non-Relativistic Kinetic Energy in Non-SI units

\[
KE[J] = \frac{m \cdot [kg] \cdot v^2 \left[ m/s \right]^2}{2} = \frac{m \cdot \left[ \frac{10^{-3} \ kg}{amu} \right] \cdot v^2 \left[ \frac{m^2 \ 10^{-4} \ cm^2}{s^2 \ m^2} \right]}{2}
\]

\[
\Rightarrow KE[J] = 8.3017 \times 10^{-32} \ m[amu] \cdot (v[cm/s])^2
\]

\[
\therefore KE[eV] = KE \left( J \cdot \frac{eV}{1.602 \times 10^{-19} J} \right) = \frac{10^{-7}}{2N_A \cdot e} \cdot mv^2 = 5.1821344 \times 10^{-13} \ m[amu] \cdot (v[cm/s])^2
\]

\[
\therefore v \cdot \left[ \frac{cm/s}{amu} \right] = \left( 2 \times 10^7 N_A e \frac{KE[eV]}{m[amu]} \right)^{\frac{1}{2}} = 1.3891389 \times 10^6 \ \frac{KE[eV]}{m[amu]}
\]

\[
\therefore T[K] = \frac{e}{k_B} E \cdot [eV] \Rightarrow v \cdot \left[ \frac{cm/s}{amu} \right] = \left( 2 \times 10^7 N_A k_B \frac{T[K]}{m} \right)^{\frac{1}{2}} = 12895 \ \frac{T[K]}{m[amu]}
\]

\[
\Rightarrow T[K] \approx 6 \times 10^{-9} \cdot m \cdot [amu] \cdot (v \cdot \left[ \frac{cm/s}{amu} \right])^2
\]

For a particle to travel less than 20% the speed of light, \( v \cdot c < 0.2 \) (faster is generally considered to require treatment with special relativity):

\[
\frac{v}{c} < 0.2 \Rightarrow \frac{KE \cdot [eV]}{m \cdot [amu]} < \frac{(c \cdot 0.2)^2}{2 \cdot e \cdot \left( \frac{N_A}{10^{-3}} \right)}
\]

\[
\frac{KE \cdot [eV]}{m \cdot [amu]} < 18.63 \times 10^6 \ \frac{eV}{amu}
\]
**APPENDIX B**

**Basic Radioactive Decay Equations and Discussion**

The following is a brief discussion on radioactive decay with some useful calculations describing the process when the decaying radioisotope is in a closed system (it is not replaced after decay and not lost before) with steady dynamics.

### B.I Summary

#### Table B1: Useful Equations for Radioactive Decay and Atom Counting

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{N(t)}{N_0} = e^{-\lambda t} )</td>
<td>General law of (radioactive) decay when the decaying unit is not replaced or lost by other means.</td>
</tr>
<tr>
<td>( \tau_{1/2} = \frac{\ln(2)}{\lambda} )</td>
<td>Relationship between half-life and decay constant.</td>
</tr>
<tr>
<td>( \tau_{1/n} = \tau_{1/2} \cdot \frac{\ln(n)}{\ln(2)} )</td>
<td>Relationship between 1/n-th-life and half-life.</td>
</tr>
<tr>
<td>( \tau = \langle t \rangle = \frac{1}{\lambda} )</td>
<td>Mean lifetime of a unit.</td>
</tr>
<tr>
<td>( \frac{\tau_{1/n}}{\ln n} = \frac{\tau_{1/m}}{\ln m} = \frac{1}{\lambda} )</td>
<td>General relationship between 1/n-th-life and 1/m-th-life.</td>
</tr>
<tr>
<td>( P_d(t) = \lambda \cdot e^{-\lambda t} )</td>
<td>Fraction of population expected to decay at time t.</td>
</tr>
<tr>
<td>( L_s(t) = (1 - \lambda) \cdot e^{-\lambda t} )</td>
<td>Fraction of population expected to survive at time t.</td>
</tr>
<tr>
<td>( \Delta N = N_0 \left( e^{-\lambda t_2} - e^{-\lambda t_1} \right) )</td>
<td>Number of expected decays between times ( t_1 ) and ( t_2 ).</td>
</tr>
<tr>
<td>( \int_{t_1}^{t_2} P_d(t) , dt )</td>
<td>( \int_{t_1}^{t_2} P_d(t) , dt )</td>
</tr>
</tbody>
</table>
B12 \[ \Delta N = N \left( \frac{\ln n}{\tau \gamma / n} \right) k \Delta t \]

Approximate number of decays expected in time \( \Delta t = t_2 - t_1 \)

For \( \frac{t \cdot \ln n}{\tau \gamma / n} \ll 1 \); \( k \) converts time units between \( t \) and \( \tau \)

Subscripts ‘u’ for unstable nuclide, ‘st’ for stable nuclide: Given \( I = \frac{N_u}{N_{st}} \), this is the amount of stable nuclide in grams [g] needed for an activity \( \frac{\Delta N_u}{\Delta t} \); \( k \) converts time units between \( t \) and \( \tau \), \( N_A \) is Avogadro’s constant and \( M_{st} \) is the mass of the stable nuclide in g/mol

B13 \[ N_{st}[g] = \left( \frac{\Delta N_u}{\Delta t} \cdot \frac{\tau \gamma / n}{\ln(n)} \cdot \frac{1}{k} \cdot \frac{1}{I} \cdot \left( \frac{M_{st}}{N_A} \right) \right) \]

B14 \[ C_u[\mu A] \approx 1.602 \times 10^{-13} \cdot \frac{C_u[\mu /]}{I} \]

With the above notation, if there is an atom flux of \( C_u \) counts per second then, given \( I \), there would be an associated flux of \( C_{st} \cdot 10^{-6} \) coulombs per second.

B15 \[ C_u[\mu A] \cdot \frac{M_{st}}{N_A} \cdot \frac{10^{-6}}{e} \cdot t[s] \]

Amount of material consumed with flux \( C_{st} \) after time \( t \) in seconds. Molar mass \( M_{st} \), \( N_A \) and \( e \) as in Table A1.

B.II Decay Constant Variability

Radioactive decay is observed to be a random process. The decay constant, \( \lambda \), describes the probability of decay within a unit of time \( \Delta t \). The half-life, \( \tau_{1/2} \), is the expected time required for the initial population, \( N_0 \), of atoms to decrease by half, \( N_0 \xrightarrow{N \rightarrow \frac{N_0}{2}} \). The mean lifetime, \( \tau \), describes the average survival time of an atom.

Although \( \lambda \), \( \tau_{1/2} \), and \( \tau \) are observed constant under a given set of circumstances, they may vary with atomic or environmental conditions such as the state of a nucleus, the local availability of electrons and the density and energy of available electromagnetic radiation. For example, an isolated neutron on Earth undergoes β⁻ decay, \( n \rightarrow p + \beta^- + \bar{\nu} \), with \( \tau_{1/2} = 618.4 \) s, while other atoms on Earth undergo β⁻ decay with a very wide range of half-lives, and stable atoms on Earth are not observed to have decaying neutrons. While disintegration times generally vary by < 1% on Earth and may be considered constant, they may vary enormously under the varied conditions of the universe (see discussion in Baum et al. 2002 p. 20 – 21).
In the case of a fully stripped nucleus, for example as a cosmic ray, electron capture is switched off. Although under terrestrial conditions $^7$Be decays by electron capture with a half life $\tau_{1/2} = 53.3$ days, the decay Q-value is too low for $\beta^+$ decay (see Appendix C) and fully ionized $^7$Be nuclei may be observed to exist for years as cosmic rays in the vacuum of space. Likewise, under normal terrestrial conditions $^{163}$Ho undergoes electron capture with $\tau_{1/2} = 4570$ years producing stable $^{163}$Dy, but fully ionized $^{163}$Dy has been experimentally observed to be unstable and undergo $\beta^−$ decay to $^{163}$Ho with $\tau_{1/2} = 47$ days (Jung et al. 1992). On the other hand, in some stars conditions may drive electron captures that would not happen on Earth, leading to the formation of neutron stars. Radiation energy and density combined with neutron density may also affect half-lives. For example, there is a low-lying isomeric excited state of $^{26}$Al with a 9.2 s mean life against $\beta^+$ decay. In some stars this state is excited and not thermalized to the ground state before the $\beta^+$ decay takes place (Ward and Fowler 1980). The much longer observed $\beta^+$ decay mean lifetime of just over 1 million years dominates decay on Earth and has particular application in exposure dating of granite rock surfaces.

B.III Basic Decay Equations

From here on, decay rates are considered constant. With $\lambda$ the constant probability of decay, the number of radioactive nuclides, $N$, of a particular radioisotope, $X$, in a closed system (no new $X$ introduced) over a series of regular time intervals, $\Delta t$, is:

$$N(t_0) = N_0$$

$$N(t_1) = N_0 - N_0 \lambda \Delta t = N_0 \left(1 - \lambda \Delta t\right)$$

$$N(t_2) = N(t_1) - N(t_1) \lambda \Delta t = N(t_1) \left(1 - \lambda \Delta t\right) = N_0 \left(1 - \lambda \Delta t\right)^2$$

Assume that the observed pattern holds for $t_n$ and show the pattern continues for $t_{n+1}$,

$$N(t_{n+1}) = N(t_n) - N(t_n) \left(1 - \lambda \Delta t\right) = N(t_n) \left(1 - \lambda \Delta t\right)^n = N(t_0) \left(1 - \lambda \Delta t\right)^n$$

By induction it is shown that for constant decay probability, $\lambda$, measured at regular time intervals of $\Delta t$, the number of nuclides remaining after $n$ intervals of $\Delta t$ is:

$$N(t_n) = N_0 \left(1 - \lambda \Delta t\right)^n$$

From the definitions, the total time lapsed by the $n^{th}$ measurement is $t_n = n \cdot \Delta t$ so that

$$N(t_n) = N_0 \left(1 - \lambda \cdot \left(t_n / n\right)\right)^n \xrightarrow{n \to \infty} N_0 e^{-\lambda t_n}, \quad \text{since} \quad \left(1 + \frac{x}{n}\right)^n \xrightarrow{n \to \infty} e^x$$

where $e$ is the base of the
natural logarithm. This is a general result for any closed system with an initial number of elements $N_0$ that decrease with constant probability $\lambda$ over a period of time $t$,

$$N(t) = N_0 e^{-\lambda t}$$

**B 2**

$$\Rightarrow \frac{N(t)}{N_0} = e^{-\lambda t}$$

The expected fraction of decayed atoms at time $t$, $D(t)/N_0$, is:

**B 3**

$$\frac{D(t)}{N_0} = \left(1 - e^{-\lambda t}\right)$$

When Rutherford and Soddy (1902a,b, 1903) published their law of radioactive decay, they derived equation B2 from the assumption that the rate of decay was proportional to the number of remaining atoms with constant of proportionality $\lambda$,

**B 4**

$$\frac{dN}{dt} = -\lambda N$$

Although over the infinitesimal time interval of $dt$ one would not expect $\lambda$ to be accurate at describing the random decay process, A4 implies:

$$dN = -N\lambda dt \Rightarrow \int_{N_0}^{N} \frac{1}{N} dN = -\lambda \int_{0}^{t} dt$$

$$\therefore \ln \left(\frac{N}{N_0}\right) = -\lambda \cdot t$$

$$\therefore \frac{N}{N_0} = e^{-\lambda t}$$

Where constants of integration are 0 assuming $N(t = 0) = N_0$. With $\lambda$ observed to be constant, A4 is the form in which Rutherford and Soddy (1902a,b, 1903) expressed their law of radioactive decay while working together at McGill University, Canada.

From B2, given a decay time $\tau_{1/n}$ for $N_0$ atoms to decay to a smaller fraction $N/N_0 = 1/n$, one may calculate $\lambda$ and vice versa:

**B 5**

$$\tau_{1/2} = -\frac{1}{\lambda} \cdot \ln \left(\frac{1}{2}\right) = \frac{\ln(2)}{\lambda}$$

Then,

$$\tau_{1/n} = \tau_{1/2} \cdot \frac{\ln(n)}{\ln(2)} = \tau_{1/2} \log_2(n)$$

**B 6**

$$\Rightarrow \frac{\tau_{1/n}}{\ln n} = \frac{\tau_{1/m}}{\ln(m)} = \frac{1}{\lambda}$$
For example, this can be used to calculate the $10^{th}$-life ($n = 10$, $\tau_{1/10}$) which is a useful time unit for radioisotope measurement since after every $10^{th}$-life, an extra order of magnitude of sensitivity is required to detect the remaining radioisotopes. It is a general rule that after 10 half-lives have elapsed, the rate of decay has sufficiently decreased to make chronology using radioisotopes in closed systems very difficult. While this number is not very intuitive, by B5 it is equivalent to $3 \times \tau_{1/10}$, or $N_0 \times 10^{-3}$ (1/1000 the initial atom population).

Since $\lambda$ represents a constant probability of decay, B2 and B3 may be used to determine the probability that an atom decays, $P_d(t)$, and the likelihood of survival, $L_s(t)$:

B 7

$$P_d(t) = \lambda e^{-\lambda t}$$

B 8

$$L_s(t) = (1 - \lambda) \cdot e^{-\lambda t}$$

As expected:

$$\int_0^\infty P_d(t)dt = 1$$
$$\int_0^\infty L_s(t)dt = 0$$

At any point in time, the expected fraction of atoms remaining at $t$ is given by B2. From B7 and B8 it is seen that at any time $P_d(t) + L_s(t) = N(t)/N_0$, the atom either decays or does not, but over infinite time the atom is expected to eventually decay and not survive. Because the second integral is 0 and not 1, the likelihood of survival may not be called a probability.

The mean lifetime, $\tau$, of a radioisotope is the expected time until it decays, $\langle t \rangle$:

B 9

$$\tau = \langle t \rangle = \int_0^\infty t \cdot P_d(t)dt = \int_0^\infty t \cdot \lambda e^{-\lambda t}dt = \frac{1}{\lambda}$$

Integration by parts ($u = t, dv = e^{-\lambda t} dt$) was used. From A6 it is seen that $\tau = \tau_{1/e}$, the $e^{th}$-life of the population: the population is $e^{-1}$ of the original population after time $\tau$.

From B7, the number of decays $\Delta N$, expected between times $t_1$ and $t_2$ is:

B 10

$$\Delta N = N_0 \int_{t_1}^{t_2} P_d(t)dt = N_0 \left( e^{-\lambda t_1} - e^{-\lambda t_2} \right)$$

as would be expected from equation B2. When $\lambda \cdot t = \frac{\ln 2}{\tau_{1/2}} \cdot t \ll 1$, one may either use a Taylor series of the above result or combine A4 and A5 for an approximation,

B 11

$$\Delta N = N \cdot \left( \frac{\ln 2}{\tau_{1/2}} \right) \cdot k \cdot \Delta t$$
Here, $\Delta N$ is the expected number of decays, $N$ is the number of atoms before $\Delta N$ have decayed, $\tau_{1/2}$ is the half-life expressed in some time unit, $\Delta t$ is the unit of time given for the decays to happen, and $k$ is a conversion factor from the time unit of $\tau_{1/2}$ to the unit of $\Delta t$. More generally,

$$\Delta N = N \cdot \left( \frac{\ln n}{\tau_{1/2}} \right) \cdot k \cdot \Delta t$$

For example, given $\tau_{1/2} = 5715$ years for $^{14}C$, $\tau = 8245$ years is the mean lifetime of a $^{14}C$ atom, $\tau_{1/10} = 18985$ years and $^{14}C$ dating by Accelerator Mass Spectrometry (AMS) has a general limit of $3 \times \tau_{1/10} = 57000$ years before present. If one wanted a count rate above 1 decay per minute $= \Delta N/\Delta t$, then $k = 1$ year/525600 minutes, and $N > 4.3 \times 10^9$ $^{14}C$ atoms would be needed.

Sometimes in geochronology and work involving radioisotope tracers, there is either a known ratio between a stable element and one of its radioisotopes, or the activity of the sample is known and the concentration of the radioisotope is desired. Let $N_u$ be the number of radioisotope atoms, $N_{st}$ the number of atoms of stable isotope atoms, and the ratio $N_u/N_{st} = I$ be known. If a certain activity, $\Delta N_u/\Delta t$, is desired, then using B12:

$$N_{st} = \frac{N_u}{I}$$

$$N_{st}[g] = \left( \frac{\Delta N_u}{\Delta t} \cdot \frac{\tau_{1/2}}{\ln(n)} \cdot \frac{1}{k} \cdot \frac{1}{I} \cdot \left( \frac{M_{st}}{N_A} \right) \right)$$

Where $N_A$ is Avogadro’s constant (~ 6.022 x $10^{23}$ units/mole), $M_{st}$ is the mass of the stable isotope in g/mol, and the term $\left( \frac{M_{st}}{N_A} \right)$ is included to express $N_{st}$ in grams of material.

Given the ratio I, if one were to look at a flux of the atoms (eg. in the ion beam of a mass spectrometer), then to achieve a count rate [c/s] of $C_u$ of the unstable ions then there would be an associated current $C_{st}$ of the stable isotope:

$$C_{st}[A] = \frac{\Delta N_{st}}{\Delta t} = \frac{1}{I} \cdot \frac{\Delta N_u}{\Delta t} = 1.602177 \times 10^{-19}[\mu A] \cdot \frac{C_u}{I}$$

$$C_{st}[\mu A] \approx 1.602 \times 10^{-13} \cdot \frac{C_u}{I}$$

The amount of stable isotope consumed in the process is
Continuing the above example using $^{14}$C, the modern ratio of $^{14}$C/C $\sim 1.2 \times 10^{-12}$. Neglecting other factors that would alter the ratio, a sample from 57 000 years before present ($3 \times 10^6$-life) would have $I \sim 10^{-15}$. Assuming 100% detection efficiency, it would take 17 hours to acquire 1000 counts of $^{14}$C at a count rate of 1 c/min.

- **Decay counting**: using B13, $> 86$ g of concentrated carbon ($M = 12$ g/mol) are needed from the sample to achieve 1 decay count per minute for $I = 10^{-15}$. The same count rate could be expected from about 1 g of concentrated carbon from a sample dating 19 000 years before present ($I = 10^{-13}$).

- **Atom counting using mass spectrometry**: using B14, 2.7 µA of stable C$^-$ for $I = 10^{-15}$ would produce 1 c/min $^{14}$C$^-$. This would consume about 20 ng of stable C per minute. Direct atom counting would then require 20 µg of material for 1000 counts $^{14}$C$^-$, more than 6 orders of magnitude less material than with decay counting. For $I = 10^{-13}$, 27 nA of stable C$^-$ would produce 1 c/min $^{14}$C$^-$, and 2.7 µA of stable C$^-$ would yield 1.7 c/s $^{14}$C$^-$, roughly 100 c/min so that 10 min would yield 1000 counts, consuming a total of 0.2 µg of stable C in the process.

In the case of rare sample material the benefits of direct atom counting are immediately obvious: orders of magnitude less material is needed and analysis times can be greatly reduced.
APPENDIX C

Beta Decay and Electron Capture

The masses of radioisotopes with $\tau_{1/2} < 1$ Ma are typically not published but are calculable if their production or decay processes are sufficiently known. Likewise, the mass of an ionized molecule or atom may be calculated if sufficient information is known about the neutral species and its ionization energy. This section provides elementary discussion and equations for $\beta^-$, $\beta^+$ and $\epsilon c$ (beta and electron capture) decays.

Throughout, $A$ is the total number of nucleons, $Z$ the number of protons (mass $m_p$) and therefore equals the number of electrons (mass $m_e$) of the neutral species, and the number of neutrons (mass $m_n$) is $N_n = A – Z$. In the notation of nuclear physics, the total mass difference between the neutral parent and neutral daughter isotope is the Q-value of the decay and $E_k$ is the maximum kinetic energy of a positron or electron during $\beta^+$ decay. Positive Q-values are exothermic, contrary to the standard formalism of chemistry where positive values represent endothermic reactions (require energy input) and negative values are exothermic (release energy).

C.I Summary

If X is a radioactive isotope with daughter Y and M is a ground state neutral mass, then the decay Q-value gives $M_x = M_Y + Q$. Also, neglecting the neutrino mass, given the maximum kinetic energy $E_k$ of a $\beta$ particle in $\beta^\pm$ decay, $E_k \leq M_X - M_Y$ for $\beta^-$, and $E_k \leq M_X - (M_Y + 2m_e)$ for $\beta^+$. If both the electron capture, $\epsilon c$, and $\beta^+$ decay channels are open, then $Q_{\epsilon c} \geq E_k(\beta^+) + 2m_e$.

C.II Beta-decay and Electron Capture

During $\beta^\pm$ decay and $\epsilon c$, A remains constant (one isotope transmutes to an isobar) but Z and $N_n$ may change. Conservation of energy, however, demands that the mass of the parent be at least slightly larger than its daughter product. The total mass difference between the neutral parent and neutral daughter isotope is the Q-value of the decay. This energy may be carried away as mass, kinetic energy, be hidden in bonding energy and so on. For $\beta^-$ and $\epsilon c$ decays, $Q \leq m_e$ may be allowed, but for $\beta^+$ decay $Q > 2m_e$ strictly, as discussed below. Any intermediate steps in the decay, for example those involving pions, will be ignored in the following summary.
An expression for the mass difference between the neutron and proton, $m_n - m_p$, expressed in terms of $m_e$, as well as an expression for the average binding energy per nucleon, $BE_n$, will be useful for the following discussion. For values and conversions not referenced, refer to Appendix A.

From Firestone and Shirley (1996, p. 1), a free neutron is unstable with $\tau_{1/2} = 618.4 \text{ s}$, 

$$n \rightarrow ^1H + \beta^- + \bar{\nu},$$

$Q_{np} = 0.782354 \pm 0.000020 \text{ MeV} \sim 1.5m_e$

The neutron is $Q_{np}$ more massive than the hydrogen atom. The rest mass of $H$ is $m_H = 1.007825032 \text{ amu}$ on the $^{12}\text{C}$ $\equiv 12 \text{ amu}$ scale (Baum et al. 2002), or $m_H = 938.7829995 \text{ MeV}$. With $m_n = 939.565346 \text{ MeV}$ and $m_e = 0.51099891 \text{ MeV}$,

$$m_H - (m_p + m_e) = -12.44eV$$

The negative sign implies that $m_H$ is less massive than a proton and electron taken separately. All atoms show this ‘mass deficiency’ and it is understood that the ‘missing mass’ is taken up as binding energy through $E = mc^2$. Whether this indicates a conversion of mass to energy via Eq 2.1, nucleon structure, nucleon and electron structure or some other phenomenon is not considered here.

In the case of $^1H$ there is only a proton-electron bond. The ionization energy of $H$ is $IE_H = 13.548443 \text{ eV}$ (Haynes and Lide 2011), about 1 eV larger than the calculated ‘missing mass’, but within the $\pm 23 \text{ eV}$ uncertainty given for $m_n$.

Nucleons are bound together by a few MeV while inner shell electrons are bound to the nucleus by less than 1 keV for smaller nuclides ($Z < 9$) and may be bound by tens of keV for larger nuclei ($Z > 27$). In any case, the ‘mass deficiency’ divided by the number of nucleons is taken to be the average binding energy per nucleon, $BE_n$:

$$BE_n \equiv \left( (Z \cdot m_H + (Z - A) \cdot m_n) - m_X \right) \cdot A^{-1}$$

Here, $m_X$ is the mass of the atom and $BE_n > 0$ for all atoms. Since $Z > 116$ has not been observed, using $m_e + m_p$ instead of $m_H$ represents another small approximation.

Finally,

$$m_n - m_p = m_e - IE_H + m_v + Q_{np} \approx m_e + Q_{np} \approx 2.5 \cdot m_e$$

The difference between the neutron mass and proton mass is about 2.5 $m_e$. 
For the following, $^{A}_{Z}X$ is the parent isotope, $Y$ is the daughter product, $M_X$ and $M_Y$ are the masses of $X$ and $Y$, $\Delta M_{XY} = M_X - M_Y$, $\Delta BE_{nXY} = BE_{nX} - BE_{nY}$. For $\beta^-$ decay and $\epsilon c$, $A$ remains constant so that one isobar transmutates to another isobar.

During $\beta^-$ decay the nucleus emits an electron and anti-neutrino, and a neutron is replaced by a proton:

$$n \rightarrow p + \beta^- + \bar{\nu}$$

$$^{A}_{Z}X \rightarrow ^{A}_{Z+1}Y + \beta^- + \bar{\nu}$$

Although $m_e$ is lost in the escaping $\beta^-$, the neutral atom $Y$ will have one more electron than $X$ did because $Y$ has an extra proton. In effect, a neutron has been replaced by a hydrogen atom. This means that $Q_{\beta^-} \approx E_k$ where $E_k$ is the maximum kinetic energy of the $\beta^-$ electron.

On the other hand, the difference in mass between the nucleons making up the nuclei of two atoms $^{A}_{Z}X$ and $^{A}_{Z+1}Y$, purely in terms of mass and neglecting differences such as binding energies, is:

$$\Delta_{A_Z M_{XY}} = (Z(m_p + m_e) + ((A - Z)m_n)) - (Z + 1)(m_p + m_e) + ((A - (Z + 1))m_n))$$

$$\therefore \Delta_{A_Z M_{XY}} = -m_p - m_e + m_n = (m_n - m_p) - m_e = (m_e + Q_{np}) - m_e = Q_{np}$$

Then,

$$\Delta BE_{nXY} = (\Delta_{A_Z M_{XY}} - \Delta M_{XY})A^{-1} = (Q_{np} - Q_{\beta^-})A^{-1}$$

Recalling that $BE_n > 0$ for all atoms, this means that if the Q-value of the $\beta^-$ decay, $Q_{\beta^-} > 0$, is less than the Q-value of the neutron $\beta^-$ decay, $Q_{np}$, then $Y$ has a weaker average binding energy per nucleon than $X$. If $Q_{\beta^-} = Q_{np}$ then $X$ and $Y$ have the same average binding per nucleon and if $Q_{\beta^-} > Q_{np}$ then $Y$ has more average binding per nucleon. For $\beta^-$ decay all three cases are possible. If $Q_{\beta^-} > A(1 + BE_{nX}) + Q_{np}$ then $Y$ would have less than 1 MeV/nucleon on average, smaller than the most loosely bound nucleus, the deuteron.

Since $Q_{\beta^-} = 0.7086$ MeV $< Q_{np}$ for $^{36}Cl \rightarrow ^{36}Ar + \beta^- + \bar{\nu}$ (Appendix E), it is clear that $BE_n$ for $^{36}Cl$ is larger than for $^{36}Ar$. Some other examples of larger parent isotope $BE_n$ for $\beta^-$ decays are $^{45}Ca$ to an excited state of $^{45}Sc$, $^{47}Sc$ to $^{47}Ti$ and $^{58}Co$ to $^{58}Ni$ with $Q_{\beta^-}$ of 0.2568, 0.6001 and 0.3815 MeV respectively (Firestone and Shirley 1996, p. 161, 257, 174).

During $\epsilon c$, an orbital electron is captured by the nucleus, a proton is replaced with a neutron, and a neutrino is emitted:

$$p + e \rightarrow n + \nu$$
The electron captured by the nucleus is lost from the electron shell. However, a neutral Y atom will have one fewer orbital electrons than X had because Y has one fewer protons than X. While the mass energy of the Y nucleus raises by at least \( m_e \), the mass-energy of the orbital electrons of Y is at least \( m_e \) less than that of X. The difference in mass between the nucleons making up the nuclei of two atoms \( {}_Z^A X \rightarrow {}_{Z-1}^A Y \), purely in terms of mass and neglecting differences such as binding energies, is:

\[
\Delta_{AZ}M_{XY} = (Z \cdot (m_p + m_e) + ((A - Z) \cdot m_n)) - ((Z - 1) \cdot m_e + ((A - (Z - 1)) \cdot m_n))
\]

\[
= m_p + m_e - m_n = m_e - (m_n - m_p) = m_e - (m_e + Q_{np}) = -Q_{np}
\]

Then,

\[
\Delta BE_{nXY} = (\Delta_{AZ}M_{XY} - \Delta M_{XY})A^{-1} = (-Q_{np} - Q_{ec})A^{-1}
\]

This means that for all \( \varepsilon c \), since \( Q_{ec} > 0 \), Y has a stronger average binding per nucleon than X. The negative sign for \( \Delta_{AZ}M_{XY} \) means that an isobar with more neutrons may be more massive than an isobar with more protons, but depending on nuclear binding energies this is not necessarily true. There are cases of both heavier neutron rich and heavier proton rich isobars among the stable elements. However, if the neutron rich isobar is a product of \( \varepsilon c \) then it will be less massive than its parent since it necessarily has stronger nuclear binding and since conservation of energy would be violated otherwise without an external source of energy. Like \( \beta^- \) decay, the parent and daughter masses need not be very different.

During \( \beta^+ \) decay, a positron and neutrino are emitted from the nucleus and a proton is replaced with a neutron:

\[
p \rightarrow n + \beta^+ + \nu
\]

\[
{}_{Z}^{A} X \rightarrow {}_{Z-1}^{A} Y + \beta^+ + \nu
\]

In this case, at least \( m_e \) has been lost from the nucleus as a positron, and Y has one fewer protons than X had so that the electron shell of a neutral Y atom will also have one fewer electrons. This is different than \( \beta^- \) decay where the nucleus loses \( 1m_e \) as a \( \beta^- \) but the electron shell gains \( 1m_e \) because there is an extra proton, and different than \( \varepsilon c \) where the electron shell loses \( 1m_e \) but the nucleus gains \( 1m_e \). During \( \beta^+ \) decay, in order to conserve energy, X must be at least 2\( m_e \) more massive than Y, 2\( m_e \leq \Delta M_{XY} = Q \) is required.

From the results above for two isotopes such that \( {}_{Z}^{A} X \rightarrow {}_{Z-1}^{A} Y \),
\[ \Delta B E_{nXY} = \left( \Delta A^2 M_{XY} - \Delta M_{XY} \right) A^{-1} = \left( -Q_{np} - Q_{\beta^+} \right) A^{-1} < \left( -Q_{np} - 2 \cdot m_e \right) A^{-1} \]

The nucleus of Y has more binding per nucleon than that of X. If the full \( Q_{\beta^+} \)-value is not known but \( E_k \) of the \( \beta^+ \) positron is known, then

\[ Q_{\beta^+} = \Delta M_{XY} \geq E_k + 2 \cdot m_e \]

Even though in both \( \beta^+ \) decay and \( \epsilon_c \) a nuclide \( X^A \) transmutes into \( Y^A \), while the \( \beta^+ \) decay channel may be closed the \( \epsilon_c \) channel may still be open.

In the case of \( ^{36}\text{Cl} \rightarrow ^{36}\text{S} \) (Appendix E), \( Q_{\epsilon_c} = 1.14207 \text{ MeV} \) and the \( E_k \) limit for a \( \beta^+ \) positron is given as \( E_k = 0.120 \text{ MeV} = Q_{\epsilon_c} - 2m_e \). Simply by knowing that there is a \( \beta^+ \) decay channel for two isobars one knows automatically that \( \Delta M_{XY} > 2m_e \).
APPENDIX D

Mass and Isobar ΔM Equations and Table

The masses of most radioisotopes are not published nor are the masses of most molecules although the masses are useful for mass spectrometry. This section provides formulae for calculating masses of neutral molecules and isotopes, mass differences between neutral isobars, and mass changes with ionization using decay Q-values, heats of formation $\Delta H$, bond dissociation energies $D$, ionization binding energy (electron affinity or ionization energy) and/or known masses $M$. In the context of this thesis, isobars are defined as atoms or compounds that have the same total number of nucleons, $A$.

D.1 Summary

Table D1 is a partial list of 74 radioisotopes, generally with $\tau_{1/2} > 10^3$, and 86 atomic and molecular isobars.

- Electron affinities were taken from Haynes and Lide (2011 section 10-156) with unlisted values represented as “NL”, and “not stable” represented with “–“.
- Half-lives, $\tau_{1/2}$, are from Firestone and Shirley (1996a, b) and Baum et al. (2002).
- The mass difference, $\Delta M$, is listed as $M_{\text{radioisotope}} - M_{\text{isobar}}$ so that negative values represent more massive isobars and vice versa, and were typically calculated using D2, D4, D6 and D8 with Q-values in Firestone and Shirley (1996a, b). In some cases for molecular isobars, D11 and D12 were used with data from Haynes and Lide (2011). The unit ‘$m_e$’ is electron mass.
- The ‘ΔM Ratio’ is ‘x’ from E11 in Appendix E and is given when multiple isobars are listed for a radioisotope. It is the ratio of $\Delta M$ for an isobar and the smallest $|\Delta M|$ listed for the set of isobars. A negative sign means that one isobar is less massive than the radioisotope and the other is more massive. Where there are multiple positive and negative $\Delta M$ values, two ‘ΔM Ratios’ are given, one using the smallest positive $\Delta M$ and one using the smallest $|\Delta M|$ of the negative values.
- Column ‘AMS Limit / note’ lists present approximate detection limits for isotopes commonly analysed by AMS as a ratio between radioisotope and stable isotope(s) of the same element (eg. $^{36}\text{Cl} / \text{Cl}$ where $\text{Cl} = ^{35}\text{Cl} + ^{37}\text{Cl}$). Letters corresponds to notes at the end of the table.
<p>| Radioisotope  | Electron Affinity (eV) | $\tau_{1/2}$ (year(s)) | Isobar  | $\Delta M$ (MeV/c²) | $\Delta M$ (m e) | $|M/\Delta M|$ | $\Delta M$ Ratio | AMS Limit / note |
|-------------|------------------------|-------------------------|---------|---------------------|----------------|----------------|----------------|----------------|
| $^3$H       | 0.75480540             | 12.33                   | $^3$He  | 0.0186              | 0.04           | 1.50 x 10⁷  | 10¹⁵           |
| $^2$H-H⁺    | -                      | -                       | $^2$Li  | 0.8618              | 1.69           | 7.57 x 10⁷  | 10¹⁵           |
| $^10$Be     | -                      | -                       | $^1$B   | 0.5560              | 1.09           | 1.68 x 10⁴   |
| $^1$C       | 1.262119               | 5715                    | $^{15}$O | -4.9866             | -9.76          | 2.62 x 10⁷   | 10¹⁶           |
| $^{12}$CH₂  | -                      | -                       | $^{13}$CH | -7.3941             | -14.47         | 1.76 x 10⁷   | 10¹⁵           |
| $^{13}$CH   | -                      | -                       | $^{15}$O | -11.5580             | -22.62         | 1.13 x 10¹   | 10¹⁶           |
| $^{12}$Al   | 0.43283                | 7.1 x 10³               | $^{26}$Mg | 4.0042              | 7.84           | 6.05 x 10⁷   | 10¹⁵           |
| $^{28}$Si   | 1.3895220              | 160                     | $^{12}$C$^{15}$N | -15.0737             | -29.50          | 1.61 x 10⁷   | 10¹⁶           |
| $^{30}$Cl   | 3.612724               | 3.01 x 10³              | $^{26}$Ar | 0.7086              | 1.39           | 4.73 x 10⁴   | 10¹⁶           |
| $^{41}$Ca   | 0.02455                | 1.03 x 10³              | $^{4}$K  | 0.4214              | 0.82           | 9.06 x 10⁴   | 10¹⁶           |
| $^{52}$Mn   | -                      | 3.7 x 10⁶               | $^{53}$Cr | 0.5970              | 1.17           | 8.27 x 10⁴   | 10¹⁵           |
| $^{65}$Zn   | -                      | 0.6679                  | $^{62}$Cu | 1.3519              | 2.65           | 4.48 x 10⁴   | 10¹⁶           |
| $^{81}$Kr   | -                      | 2.3 x 10⁸               | $^{81}$Br | 0.2807              | 0.55           | 2.69 x 10⁸   | 10¹⁶           |
| $^{90}$Sr   | 0.048                  | 28.78                   | $^{90}$Zr | 2.8282              | 5.53           | 2.96 x 10⁶   | 10¹⁶           |
| $^{99}$Mo   | 0.893                  | 700                     | $^{91}$Zr | 1.2530              | 2.45           | 6.77 x 10⁵   | 10¹⁶           |
| $^{133}$Cs  | 0.471626               | 2.3 x 10⁶               | $^{125}$Ba | 1.05                | 1.01           | 2.40 x 10⁵   | 10¹⁶           |</p>
<table>
<thead>
<tr>
<th>Radioisotope</th>
<th>Electron Affinity (eV)</th>
<th>$\tau_{1/2}$ (year(s))</th>
<th>Isobar</th>
<th>$\Delta M$ (MeV/$c^2$)</th>
<th>$\Delta M$ (m_e)</th>
<th></th>
<th>$\Delta M$</th>
<th>AMS Ratio</th>
<th>AMS Limit / note</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{137}$Cs</td>
<td>0.471626</td>
<td>30.07</td>
<td></td>
<td>$^{137}$Ba</td>
<td>1.1756</td>
<td>2.30</td>
<td>1.09 x 10^5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{137}$La</td>
<td>0.47</td>
<td>$6 \times 10^4$</td>
<td></td>
<td>$^{137}$Ba</td>
<td>0.6000</td>
<td>1.17</td>
<td>2.13 x 10^8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{136}$Sm</td>
<td>NL</td>
<td>$1.03 \times 10^8$</td>
<td>$^{136}$Nd</td>
<td>0.0700</td>
<td>0.14</td>
<td>1.94 x 10^5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{142}$Sm</td>
<td>NL</td>
<td>$1.06 \times 10^{11}$</td>
<td>$^{142}$SnO_2</td>
<td>&lt; 20.2300</td>
<td>&lt; 39.59</td>
<td>6.72 x 10^5</td>
<td>c</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{140}$Sm</td>
<td>NL</td>
<td>7 x $10^{15}$</td>
<td>$^{140}$Nd</td>
<td>1.9291</td>
<td>3.78</td>
<td>7.15 x 10^5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{151}$Sm</td>
<td>NL</td>
<td>90</td>
<td>$^{151}$Eu</td>
<td>0.0770</td>
<td>0.15</td>
<td>1.83 x 10^8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{150}$Gd</td>
<td>NL</td>
<td></td>
<td>$^{150}$Sm</td>
<td>1.2900</td>
<td>2.52</td>
<td>1.08 x 10^5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{154}$Dy</td>
<td>NL</td>
<td>3 x $10^6$</td>
<td>$^{154}$Sm</td>
<td>2.0633</td>
<td>4.04</td>
<td>6.95 x 10^5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{152}$Gd</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{182}$Hf</td>
<td>&gt;&gt;0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{194}$Hg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{208}$Pb</td>
<td>0.364</td>
<td>5.3 x $10^4$</td>
<td>$^{208}$Pb</td>
<td>1.4140</td>
<td>2.77</td>
<td>1.33 x 10^5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{208}$Pb</td>
<td>0.364</td>
<td>$1.5 \times 10^6$</td>
<td>$^{208}$Pb</td>
<td>0.0512</td>
<td>0.10</td>
<td>3.73 x 10^6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>22.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{207}$Bi</td>
<td>0.942362</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{206}$Pb</td>
<td>0.942362</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{209}$Po</td>
<td>1.9</td>
<td>102</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Other Shorter-lived but Possibly Useful Systems**

<table>
<thead>
<tr>
<th>Pm</th>
<th>NL</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Eu</th>
<th>0.864</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Gd</th>
<th>NL</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


### Table D1: Properties of Radioisotopes and Isobars

| Radioisotope | Electron Affinity (eV) | $\tau_{1/2}$ (year(s)) | Isobar | $\Delta M$ (MeV/c$^2$) | $\Delta M$ (me) | $|M/\Delta M|$ | $\Delta M$ Ratio | AMS Limit / note |
|--------------|------------------------|------------------------|--------|-------------------------|----------------|----------------|----------------|-----------------|
| Tb 157       | NL                     | 70                     | 157Gd  | 0.0601                  | 0.12           | 2.43 x 10$^6$ |                 |                 |
| Tb 158       | 180                    | 158Dy                  |        | 0.9368                  | 1.83           | 1.57 x 10$^7$ |                 |                 |
|              |                        | 158Gd                  |        | 1.2200                  | 2.39           | 1.21 x 10$^8$ | 1.3            |                 |

Notes: a) $^{14}$O $\tau_{1/2} = 70.606$ s; b) Used $M = 3 \times M(^{12}$C), should be within 30 eV of the actual $^{12}$C$_3$ mass; c) used $M = M(^{115}$Sn) + 2 x M($^{16}$O), should be within 30 eV of the actual mass.

### Figure D1: Ranges of Values for $\Delta M$ and $M / \Delta M$ from Table D1

The bar graphs are based on Table D1 with symbols defined therein: $\Delta M_{XY}$ is the mass difference between a radioisotope listed in the first column and one of its isobars, and ‘me’ means the units are in terms of electron mass. Percentages are given for atomic isobars only, all molecular data is excluded.
### D.II Mass and ΔM Equations

Nuclear binding energies per nucleon, BEₙ (Appendix C), are on the order of MeV (> 2 mₑ) while molecular bonds are usually < 10 eV (< 2 x 10⁻⁵ mₑ) which is not surprising considering the atomic binding energies of valence shell electrons. The difference in mass deficiency between neighbouring elements is typically a few MeV (= a few milli-amu), but may be tens of MeV for elements separated by larger ΔZ. In table D1, atomic Isobars are closer in mass than atomic and molecular isobars, and, as expected, isobars with ΔZ = 1 are closest.

First, if A is a radioisotope that decays to B, then the Q-value is defined as

\[ M_A = M_B + Q \]
\[ \Delta M_{AB} = Q \]

with A and B neutral and in their ground states.

If A decays to C in a series such as \( A \xrightarrow{Q_1} B_{1} \xrightarrow{Q_2} B_{2} \ldots \xrightarrow{Q_n} C \) then,

\[ M_A = M_C + \sum_{i} Q_i \]
\[ \Delta M_{AC} = \sum_{i} Q_i \]

From D1 it follows that if A decays to B via one channel (eg. β⁻ decay) and to C via another channel (eg. εc) with associated Q-values Q_{AB} and Q_{AC} respectively, then:

\[ M_B = M_C + (Q_{AC} - Q_{AB}) \]
\[ \Delta M_{BC} = Q_{AC} - Q_{AB} \]

Then, if isotopes A and Z each had two decay channels with series

\[ B \leftarrow Q'(A'_{m+1}) \leftarrow A'_n \leftarrow Q'(A'_n) \ldots A'_1 \leftarrow Q'(A'_1) \rightarrow A_{m} \rightarrow Q(A_m) \rightarrow C \]
\[ C \leftarrow Q'(Z'_{p+1}) \leftarrow Z'_p \leftarrow Q(Z'_p) \ldots Z'_1 \leftarrow Q(Z'_1) \rightarrow Z_{q} \rightarrow Q(Z_{q+1}) \rightarrow Y \]

Then,

\[ \Delta M_{AZ} = \sum_{i=1}^{m+1} Q(A_i) - \sum_{i=1}^{p+1} Q(Z'_i) \]
\[ \Delta M_{YB} = \sum_{i=1}^{n+1} Q(A'_i) - \sum_{i=1}^{m+1} Q(A_i) + \sum_{i=1}^{p+1} Q(Z'_i) - \sum_{i=1}^{q+1} Q(Z_i) \]

A molecule XY will have different mass than X and Y separately due to bonding energy:

\[ M_{XY} = M_X + M_Y - D(X - Y) \]

Alternatively,
\[ D(X - Y) = \Delta_f H(X) + \Delta_f H(Y) - \Delta_f H(XY) \]

\[ \Rightarrow M_{XY} = M_X + M_Y - \Delta_f H(X) - \Delta_f H(Y) + \Delta_f H(XY) \]

On the other hand, if one or both of X and Y are themselves compound, e.g., Y = WZ, but only the values for D11 are known then the calculation is still valid for M_{XY} and the individual bond dissociation energies for each bond of the X and Y compounds are not needed. This is analogous to the nuclear mass deficiency that is accounted for by nuclear binding described in Appendix C.

Ionization of a neutral atom or molecule may result from addition or removal of electrons or ions. Again, the binding energy must be considered in calculating the mass of the ionized atom or molecule. In the case of a neutral X ionized by addition or removal of particles Y_i (1 \leq i \leq n, integer) with charge q, with the i^{th} particle bound by binding energy B(Y_i),

\[ M_{X^{\pm q}} = M_X \pm n \cdot M_Y \mp \sum_{i=1}^{n} B(Y_i) \]

Upper signs represent ionization by particle addition while lower signs are for particle removal. If Y is an electron then for singly charged anions and cations,

\[ M_{X^-} = M_X + m_e - EA(X) \]

\[ M_{X^+} = M_X - m_e + IE(X) \]

where EA(X) and IE(X) are the electron affinity and ionization energy of X respectively.
**APPENDIX E**

**Curve Shapes**

E.1 **Summary**

A Gaussian distribution is given as the idealized peak shape for a mass spectrum measured by a mass spectrometer with constant resolving power $R = M/\Delta M$ such that the peak width is $\Delta M = 2\delta$ given at some fraction of the peak height $0 < h < 1$ (eg. if $2\delta$ is the full width at half maximum, FWHM, $h = 0.5$). Care should be taken when discussing resolving power as some uses define $\Delta M = \Delta M_{XY} = |M_X - M_Y|$ where $X$ and $Y$ are the closest neighbouring peaks of equal intensity that can be resolved at some value $h$ of the peak height, as discussed at the time of writing at IUPAC (2011). In this section all peaks are considered Gaussian and all background is assumed due to tails from other peaks.

For a series of measurements $x_n$ with average value $\langle x_n \rangle = \mu$ the variance is defined as:

\[
\sigma^2 = \lim_{N \to \infty} \frac{1}{N} \sum_{n=1}^{N} (x_n - \mu)^2
\]

A Gaussian distribution has the general form:

\[
g_n(x, \mu, \sigma) = \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}
\]

Which may also be expressed with mass, $m$, centred at the mass of isotope $X$ ($M_X$) as:

\[
H(m, M_X, R) = H_0 \cdot h^{(2R)^2 \left(\frac{m}{M_X}\right)^2}
\]

since

\[
\therefore \delta = \sigma \sqrt{2\ln(h^{-1})}
\]

At a fraction $f$ of the peak height, the half-width $\phi$ is related to $\delta$ by:

\[
\phi = \delta \sqrt{\frac{\ln(f^{-1})}{\ln(h^{-1})}} = \delta \sqrt{\frac{\ln f}{\ln h}}
\]

and

\[
f = h \left(\frac{\phi}{\delta}\right)^2
\]

For $2\delta =$ FWHM, $E5 \Rightarrow \phi = 1.82 \sqrt{\log_{10} f} \cdot \delta$.

To resolve two isobars $X$ and $Y$ with relative abundance $I_Y / I_X = I_{YX} \leq 1$,
If $Y$ is to be resolved at $b$ times the background, $u^{-1} = (2b)$.

Suppose there were a third isobar $Z$. If $M_X < M_Y < M_Z$ or vice versa, $R \geq \text{maximum}(R_X, R_Z)$ as given by E9 would be needed for resolution. Otherwise, take $|\Delta M_{XY}| < |\Delta M_{ZY}|$ and define:

$$E_{11}$$

$$x = \frac{|\Delta M_{ZY}|}{|\Delta M_{XY}|}$$

When $x < \frac{|M_Y/\Delta M_{XY}|}{10}$ (for example $x < 10$, $|M_Y/\Delta M_{XY}| > 1000$, otherwise see E13 – E15), if

$$E_{17}$$

$$I_{XZ} > \left(u \cdot I_{YX}\right)^{x^{-1}}$$

then $R_X$ will not be sufficient for resolution of $Z$ from $Y$. Here, $I_{XZ} = I_X / I_Z$ is the relative abundance of $X$ to $Z$, and similarly $I_Y / I_X = I_{YX}$. This approximation is appropriate for all of the atomic isobars of table D1. In general, for $x > 1.4$, $I_{XZ} << 1$ ($Z$ must be orders of magnitude more abundant than $X$) before $R_X$ is insufficient for resolution of $X$ and $Z$ from $Y$.

Table E1 can be used with table D1 to make quick estimates of resolution and to compare resolutions needed for different $I_{YX}$ (with the idealizations of this section). For example, only about 3 times the resolving power is needed at $I_{YX} = 10^{-20}$ than is needed for $I_{YX} = 1$ under these idealized conditions.

### E.II Introduction

Low abundance ratio measurements ($\leq 10^{-12}$) present a multitude of challenges, and adjusting to the sub-parts-per-trillion universe is not always intuitive. Several processes including scattering, charge exchange, ionization-induced and Boltzmann ion energy spreads, and molecular break-up may lead to false identifications during a mass spectrometry (MS) measurement of a rare isotope in the presence of neighbouring and relatively abundant isobars. As more sensitive abundance ratios are desired, interferences from neighbouring isobars become harder to resolve.

Rather than assigning individual uncertainties to phenomena that may have a random nature during any given measurement, an overall Gaussian uncertainty distribution will be used to model peak shapes in mass spectra based on mass a spectrometer resolving power $R = M/\Delta M$. 
Given a mass $M$, the width of the detected peak centred at $M$ will be $\Delta M = M/R$ wide at some fraction of the peak height, $h$ (eg. $h = \frac{1}{2}$ at full width half maximum, FWHM). Note that there is ambiguity with the definition of $R$ as some use $\Delta M = \Delta M_{XY} = |M_X - M_Y|$ where $X$ and $Y$ are the closest neighbouring peaks of equal intensity that can be resolved at some value $h$ of the peak height (IUPAC 2011).

The problem: Given two isobars $X$ and $Y$ that have a mass difference $\Delta M_{XY}$ and an abundance ratio $I_Y/I_X = I_{XY} \leq 1$, what is the minimum resolving power, $R (=M/\Delta M$, assumed a constant of the instrument), needed in order to sufficiently resolve both $X$ and $Y$ as individual peaks? Then, how would the presence of a third isobar $Z$ with relative abundance $I_{YZ} \leq 1$ such that $|\Delta M_{XY}| < |\Delta M_{ZY}|$ affect the requirements on $R$? A Gaussian peak shape is only an approximation to actually observed distributions, which are typically asymmetric with ‘tails’. A Gaussian distribution is a good approximation near the peak, $H_0$, however actual peaks will likely be ‘wider’ or less resolved than a Gaussian peak at values further from $H_0$ in MS.

**E.III Basic Definitions and Discussion on Gaussian Distributions**

A full derivation and justification for the ‘Gaussian’, ‘normal’ or ‘error’ distribution will not be given. Many different approaches exist (eg. Poincaré 1912 p. 169 – 189, and discussion in other chapters) but while all are fairly interesting overall, they are generally tedious in the details. For certain, given the assumptions about the set of possible observations discussed below, the Gaussian error function describes the distribution. On the other hand, as Poincaré himself points out regarding its general use in experimental analysis (Poincaré 1912 p. 170 – 171),

> « Elle [‘la loi des erreurs’] ne s’obtient pas par des déductions rigoureuses; plus d’une démonstration qu’on a voulu en donner est grossière,… Tout le monde y croit cependant, me [Henri Poincaré] disait un jour M. Lippmann, car les expérimentateurs s’imaginent que c’est un théorème de mathématiques, et les mathématiciens que c’est un fait expérimental. »

> “It [‘the law of errors’] is not obtained by rigorous deductions; more than one demonstration hoped to produce it is rough,… However, everyone believes in it, Mr. Lippmann told me [Henri Poincaré] one day, experimenters believe it as a mathematical theorem, and mathematicians as an experimental fact.”

A Gaussian distribution describes a set of random variables that are rotationally invariant, statistically independent and continuous, but it may also be used to approximate conditions for a discrete set of variables. Experimentally, it is assumed that measured values $x_n$ of a parameter under constant conditions are statistically independent (accounting for systematic errors separately). Independence of $x_p$ and $x_q$ means,

$$P(x_p \cap x_q) = P(x_p)P(x_q)$$
As a distribution of experimental observations, it is also supposed that the measured values converge to something approaching the ‘true’ value but that any one measurement will deviate due to associated errors. That is, the series converges to an average or expected value, $\langle x \rangle = \mu$, in the limit of many, $N$, measurements,

$$E \quad \langle x \rangle = \lim_{N \to \infty} \frac{1}{N} \sum_{n=1}^{N} x_n \rightarrow \mu$$

Values such as mass, momentum, time or energy are assumed knowable to an accuracy not exceeding the limits of the Heisenberg Uncertainty Principle and the value obtained by any set of observations is assumed random. There is also no assumed asymmetry in the observation space containing all possible observed values, and the values themselves are assumed invariant under rotations; the $x_n$ are not vectors. The space has an associated density function, $f_n(x)$, such that $\int_{-\infty}^{\infty} f_n(x) \, dx = 1$. It may be used to find the probability that an observation will fall between different values, $P(a \leq x \leq b) = \int_{a}^{b} f_n(x) \, dx$. Because of the assumed symmetry and randomness,

$$\sum_{n}^{N} (x_n - \mu) \rightarrow_{N \to \infty} 0$$

In order to quantify the fluctuation of measurements, which may indicate the reliability of data, one may want to know on average ‘how far’ $x_n$ is from the ‘true’ or expected value $\mu$. The absolute value, $|x_n - \mu|$, could be used, or a term appropriately named the ‘variance’, $\sigma$, which is more easily used mathematically may be defined:

$$E \quad \sigma^2 \equiv \lim_{N \to \infty} \sum_{n}^{N} (x_n - \mu)^2$$

The density function, $g_n(x)$, that satisfies all of the above is,

$$E \quad g_n(x, \mu, \sigma) = \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{1}{2} \left( \frac{x-\mu}{\sigma} \right)^2}$$

This is the Gaussian function. The Fourier transform of $g_n(x)$, $G_n(y)$, when $\mu = 0$ is,

$$G_n(y, 0, \sigma) = \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{1}{2} \left( \frac{\sigma^{-1} y}{\sigma} \right)^2}$$

So that $\sigma_y = 1/\sigma_x$. In general, a Fourier transform pair obeys $\sigma_x \sigma_y \geq 1$. The two functions, $g_n(x)$ and $G_n(y)$ are two different ways to parameterize the same distribution, for example in time and
frequency. As one parameter $x$ is more defined, the parameter $y$ is less well defined and this is more or less the Heisenberg Uncertainty Principle.

### E.IV Gaussian Curve Calculations

The following is based on a measured peak with distribution described by $E\, 3$ and maximum height $H_0$. First, at the position $x = \mu \pm \sigma$, $H_0(x = \mu \pm \sigma, \mu, \sigma) = e^{-1/2} H_0$. At what position $x = \mu \pm \delta$ is the curve a fraction $h$ ($0 < h < 1$) of the maximum $H_0$ ($H_0/H_0 = h$)? That is, at what position $x = \mu \pm \delta$ does $y = H_\delta = h \cdot H_0$? From $E\, 3$,

$$H_0 = H(\mu, \mu, \sigma) = g(\mu) = \frac{1}{\sigma \sqrt{2\pi}}$$

$$H_\delta(\mu + \delta, \mu, \sigma) = g(\mu + \delta) = \frac{1}{\sigma \sqrt{2\pi}} e^{-1/2} \left(\frac{\delta}{\sigma}\right)^2 = h \cdot H_0 = \frac{h}{\sigma \sqrt{2\pi}}$$

\[E\, 4\]

Given $\delta$ and $h$, the point $x = \mu \pm \phi$ at which an attenuation $0 < f < 1$ occurs is then:

\[E\, 5\]

$$\phi = \delta \sqrt{\frac{\ln(f^{-1})}{\ln(h^{-1})}} = \delta \sqrt{\frac{\ln f}{\ln h}}$$

\[E\, 6\]

Since \( \frac{\ln f}{\ln a} = \log_a f \), for $h = 0.5$ (e.g. $2\delta =$ FWHM), $E\, 5 \Rightarrow \phi = 1.82 \cdot \delta \sqrt{\log_{10}(f^{-1})}$. Instead of using $\sigma$, $\delta$ may be used to define the distribution:

$$H(x, \mu, \delta) = \frac{1}{\delta} \sqrt{\frac{\ln(h^{-1})}{\pi}} e^{-\ln(h^{-1}) \left(\frac{x-\mu}{\delta}\right)^2} = \frac{1}{\delta} \sqrt{\frac{\ln(h^{-1})}{\pi}} \cdot h^{\left(\frac{x-\mu}{\delta}\right)^2}$$

\[E\, 7\]

$$\Rightarrow H(x, \mu, \delta) = H_{x=0} \cdot h^{\left(\frac{x-\mu}{\delta}\right)^2}$$

This is $E\, 6$ expressed in terms of $x$ instead of $x = \mu \pm \phi$. To get $E\, 3$, $h = e^{-1/2}$ and $\delta = \sigma$. As an example, if the FWHM = $\Delta$ ($h = \frac{1}{2}$), then $H_{\Delta/2} = H_0/2$ occurs at $x = \mu \pm \Delta/2$, $\sigma \approx 0.425 \Delta$, and at 5 times this distance, $H(\mu \pm (5\Delta/2), \mu, \Delta/2)/H_0 = f = 0.5^{25} = 3 \times 10^{-8}$.

### E.V Gaussian Curve Interferences Between Two Isobars

In accordance with the conventions used above, let $X$ and $Y$ be two isobars with masses $M_X$ and $M_Y$, mass difference $\Delta M_{XY} = M_Y - M_X$, abundances $I_X$ and $I_Y$ and relative abundance
I_{YX} = I_Y/I_X \leq 1. The isobar of interest is Y and a mass spectrometer with constant resolving power \( R = M/\Delta M \) at fraction \( 0 < h < 1 \) of the maximum peak height \( H_0 \) will be used to resolve Y from X. Peaks are considered Gaussian with width at \( h \cdot H_0 \) of \( \Delta M = 2\delta = M/\sqrt{R} \).

There are two Gaussian curves, \( H_{m-\mu}^X(m, M_X, \delta) \) for X and \( H_{m-\mu}^Y(m, M_X + \Delta M_{XY}, \delta) \) for Y, where H represents the measured abundance as opposed to the theoretical abundance I, at a given mass m. Resolution of Y typically demands that \( H_Y \) must be at least 3 times the background, assumed all due to X. All curves will add constructively at any given point so the distance \( \varphi_u^Y \) is needed such that \( H_{\varphi}^Y(M_X + \Delta M_{XY} - \varphi_u^Y, M_X + \Delta M_{XY}, \delta) = u \cdot H_0^Y \leq H_0^{\delta^Y} \), where Y is assumed more massive than X so that if this relation holds at \( M_X + \Delta M_{XY} - \varphi_u^Y \) then it will also hold at \( M_X + \Delta M_{XY} + \varphi_u^Y \) because the peaks are Gaussian. The case \( M_Y < M_X \) is analogous.

From E5,

\[
\varphi_u^Y = \delta^Y \left( \frac{\ln(u)}{\ln(h)} \right)
\]

Resolution of Y may now be stated as \( H_X^Y (M_X + \Delta M_{XY} - \varphi_u^Y, M_X, \delta) \leq u \cdot H_0^Y \). From E7:

\[
H_{\varphi}^X = H_X^Y (M_X + \Delta M_{XY} - \varphi_u^Y, M_X, \delta) = H_0^X h \left( \frac{\Delta M_{XY} - \varphi_u^Y}{\delta^X} \right) \leq u \cdot H_0^Y
\]

Since the exponent is squared and \( 0 < \frac{H_0^Y}{H_0^X} = 1_{YX}, u, h \leq 1 \), inverses should be used,

\[
\Rightarrow -\ln(u \cdot I_{YX}) \leq -\left( \frac{\Delta M_{XY} - \varphi_u^Y}{\delta^X} \right) \ln(h)
\]

\[
\Rightarrow \sqrt{\frac{\ln(u \cdot I_{YX})}{\ln(h^{-1})}} \leq \frac{\Delta M_{XY} - \varphi_u^Y}{\delta^X} \sqrt{\frac{\ln(u^{-1})}{\ln(h^{-1})}}
\]

From the definition of resolving power, \( 2\delta^X = \frac{M_X}{R} \) and \( 2\delta^Y = \frac{M_X + \Delta M_{XY}}{R} \),

\[
\Rightarrow \frac{\Delta M_{XY}}{M_X} = 1 + \frac{\Delta M_{XY}}{M_X}
\]

\[
\Rightarrow \sqrt{\frac{\ln(u \cdot I_{YX})}{\ln(h^{-1})}} + \sqrt{\frac{\ln(u^{-1})}{\ln(h^{-1})}} \left( 1 + \frac{\Delta M_{XY}}{M_X} \right) \leq \frac{\Delta M_{XY}}{M_X}
\]
Since by assumption $\Delta M_{XY} > 0$, 

**E 8** \[ R \geq \frac{1}{2 \sqrt{\ln(h^{-1})}} \cdot \left| \frac{M_X}{\Delta M_{XY}} \right| \left( \sqrt{\ln\left(\frac{u \cdot I_{XY}}{I_X} \right)^{-1}} + \sqrt{\ln\left(\frac{u^{-1}}{I_Y} \right)^{-1}} + \frac{\Delta M_{XY}}{M_X} \sqrt{\ln\left(\frac{u^{-1}}{I_Y} \right)} \right) \]

**E 9** \[ \approx \frac{1}{2 \sqrt{\ln(h^{-1})}} \cdot \left| \frac{M_X}{\Delta M_{XY}} \right| \left( \sqrt{\ln\left(\frac{u \cdot I_{XY}}{I_X} \right)^{-1}} + \sqrt{\ln\left(\frac{u^{-1}}{I_Y} \right)^{-1}} \right) \]

With this $R$, at $\phi_h$ the total height of the curve is $H_h = H_{\phi} = H^{X}_{\phi} + H^{Y}_{\phi} = H^{X}_{\phi} + u \cdot H^{Y}_0 \leq 2 \cdot u \cdot H^{Y}_0$ if all background is due to the peak of X. Then, if $u = 1/6$, Y will be resolved at $\geq 3$ times the background. In general, if Y is to be resolved at $b$ times the background then $u^{-1} = (2b)$ since E9 accounted for 2 isobars. In the special case $I_{YX} = 1$, E9 resembles E5 with the first term dictating the peak width and the second term representing the separation. Using $\Delta M = \frac{M}{R} = 2\delta$ (see first paragraph of this section for definition), E7 may be re-written in terms of $R$ and $M_X$:

**E 10** \[ H(m, M_X, R) = H_0 \cdot h^{(2R)^2 \cdot \left\{ \frac{m}{M_X} \right\}^{-1}} \]

Again, $M_X$ is the mass of isotope X and R is the resolving power at $\delta$ (see E5) such that $H^{X}_{\delta} = h \cdot H^{X}_0 < H^{X}_0$ (eg. $h = \frac{1}{2}$ at FWHM); $m = M_X \pm \Delta M_{XY}$ is the mass of Y.

Comparing equations E9 and E5 an interesting feature comes to light. Consider E5 with two peaks for X and Y such that $H^{Y}_{0} / H^{X}_{0} = I_{YX} = 10^{-8} = f$ (eg. $H^{X}_{\delta} = H^{X}(M_X + \Delta M_{XY}) = f \cdot H^{X}_0$) and $\delta$ at FWHM so that $h = 0.5$. According to E5, the Gaussian distribution of X is 5.2$\delta$ at Y, the distribution of X is over 5 times wider than the FWHM value at the position of the peak of the Y distribution. In order to resolve these two peaks one might expect to need over 5 times more resolving power, R, than is needed if $I_{YX} = 1$. However, if the peaks were truly Gaussian then as R increased both peaks would ‘exponentially squeeze’. Using E9 with $u = 1/6$ ($H^{Y}_0 \geq 3$ times the background) and calculating $R(I_{YX} = 10^{-8}) / R(I_{YX} = 1)$, if the peaks were truly Gaussian then only 2.2 times the resolving power needed for $I_{YX} = 1$ is needed for resolution of Y from X when $I_{YX} = 10^{-8}$. This is illustrated in figure E1 and values for $R \cdot \left| \Delta M_{XY} / M \right|$ versus $I_X / I_Y = (I_{YX})^{-1}$ are listed in table E1 for quick calculation given arbitrary $| M / \Delta M_{XY} |$.

Figure E2 illustrates the changes in resolving power (at FWHM) demands versus isobar mass difference, $| \Delta M_{XY} |$ (given in electron masses $m_e$), for 4 different relative abundances $I_{YX}$ using the example of $M = 36$ and calculated using E9 with $u^{-1} = 6$. Generally, when isobars are
within $|\Delta M_{XY}| \leq 20m_e$ and $I_{YX} < 1$, high $R > 10^4$ is needed; for $|\Delta M_{XY}| < 0.2m_e$, $R > 10^6$ is needed and $R > 10^5$ is needed up to 1.6$m_e$. In figure D1, $|\Delta M_{XY}| \leq 10m_e$ for all of the atomic isobars while $|\Delta M_{XY}| \leq 20m_e$ for only 3 of the 13 tabulated molecular isobars. In the case of $^{36}$Cl, 2 atomic and 2 molecular isobars are listed in Table D1. For the atomic isobars $|\Delta M_{XY}| \leq 2.5m_e$, and if $I_{YX} = 10^{-6}$ a resolving power approaching $10^6$ would be needed.

**Figure E 1: Resolving Power and Relative Abundance for $|M/\Delta M_{XY}| = 1000$**

This figure illustrates the changes in resolving power, $R$ (given here at full width half maximum, FWHM), requirements for resolution of two isobars, $X$ and $Y$, as the relative abundance, $I_Y/I_X = I_{YX}$, changes, assuming Gaussian peaks (E10). When $M/\Delta M_{XY} = 10^3$ and $I_{YX} = 1$ the two isobars may be resolved with $R_1 = 1610$, shown on top. When $I_{YX} = 10^{-8}$, $R_2 \geq 2.18R_1 \sim 3500$ is needed (shown below) since if $R_1$ is used the peak of $Y$ will be buried by 5 orders of magnitude from the tail of $X$. 
Figure E 2: Resolving Power R vs. Isobar Mass Difference $|\Delta M_{XY}|$ for $M = 36$ amu

The minimum resolving power $R$ to separate isobars $X$ and $Y$ is tabulated using E9 for four different isobar ratios, $I_Y / I_X = I_{YX}$, and plotted against isobar mass difference $|\Delta M_{XY}|$ (given in units of electron mass $m_e$) for $M=36$, $h = 0.5$ (FWHM) and $u = 1/6$. 

Relative Abundance of $Y$ to $X$, $I_Y / I_X = I_{YX}$:

- $10^{-12}$
- $10^{-6}$
- $10^{-2}$
- $1$
Table E 1: Resolving Power R vs. Relative Abundance \((I_{YX})^{-1}\)

<table>
<thead>
<tr>
<th>(u^{-1})</th>
<th>(h^{-1})</th>
<th>(\text{FWHM})</th>
<th>10% valley</th>
<th>5% valley</th>
<th>(R_{FWHM} \cdot \frac{\Delta M}{M})</th>
<th>(R_{0.1} \cdot \frac{\Delta M}{M})</th>
<th>(R_{0.05} \cdot \frac{\Delta M}{M})</th>
<th>(\frac{R}{R_0})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td>1.61</td>
<td>0.88</td>
<td>0.77</td>
<td>1.00</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.02</td>
<td>1.11</td>
<td>0.97</td>
<td>1.26</td>
</tr>
<tr>
<td>10^2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.32</td>
<td>1.27</td>
<td>1.12</td>
<td>1.44</td>
</tr>
<tr>
<td>10^3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.58</td>
<td>1.41</td>
<td>1.24</td>
<td>1.60</td>
</tr>
<tr>
<td>10^4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.80</td>
<td>1.53</td>
<td>1.34</td>
<td>1.74</td>
</tr>
<tr>
<td>10^5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.99</td>
<td>1.64</td>
<td>1.44</td>
<td>1.86</td>
</tr>
<tr>
<td>10^6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.18</td>
<td>1.74</td>
<td>1.53</td>
<td>1.98</td>
</tr>
<tr>
<td>10^7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.35</td>
<td>1.84</td>
<td>1.61</td>
<td>2.08</td>
</tr>
<tr>
<td>10^8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.50</td>
<td>1.92</td>
<td>1.69</td>
<td>2.18</td>
</tr>
<tr>
<td>10^9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.65</td>
<td>2.00</td>
<td>1.76</td>
<td>2.27</td>
</tr>
<tr>
<td>10^10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.80</td>
<td>2.08</td>
<td>1.83</td>
<td>2.36</td>
</tr>
<tr>
<td>10^11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.93</td>
<td>2.16</td>
<td>1.89</td>
<td>2.45</td>
</tr>
<tr>
<td>10^12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.06</td>
<td>2.23</td>
<td>1.95</td>
<td>2.53</td>
</tr>
<tr>
<td>10^13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.19</td>
<td>2.30</td>
<td>2.01</td>
<td>2.60</td>
</tr>
<tr>
<td>10^14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.31</td>
<td>2.36</td>
<td>2.07</td>
<td>2.68</td>
</tr>
<tr>
<td>10^15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.42</td>
<td>2.43</td>
<td>2.13</td>
<td>2.75</td>
</tr>
<tr>
<td>10^16</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.54</td>
<td>2.49</td>
<td>2.18</td>
<td>2.82</td>
</tr>
<tr>
<td>10^17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.65</td>
<td>2.55</td>
<td>2.23</td>
<td>2.89</td>
</tr>
<tr>
<td>10^18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.75</td>
<td>2.61</td>
<td>2.29</td>
<td>2.96</td>
</tr>
<tr>
<td>10^19</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.86</td>
<td>2.66</td>
<td>2.34</td>
<td>3.02</td>
</tr>
<tr>
<td>10^20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.96</td>
<td>2.72</td>
<td>2.38</td>
<td>3.08</td>
</tr>
</tbody>
</table>

Equation E 9 was used to calculate the resolving powers, R, needed to resolve isobars X and Y with relative abundance \(I_Y / I_X = I_{YX} \leq 1\) and mass difference \(\Delta M\) (to get R, multiply the value by a given \(|M/\Delta M|\); e.g. \(10^3\) for figure E1). Resolution of the minor peak above the background tail of the major peak is given by \((2u)^{-1}\) (e.g. \(u^{-1} = 6\) means the minor peak is 3 times background, see E 9). For \(h\) also see E 4; here it indicates at what percent of the peak maximum the resolving power is defined. In the last column, \(R_0 = R(I_{YX}^{-1} = 1)\); only 3.08 times the resolving power is needed for \(I_{XY} = 1\) is needed for \(I_{XY} = 10^{-20}\).

Now suppose there were two isobars X and Z requiring \(R_X\) and \(R_Z\) for resolution from Y. In the case \(M_X < M_Y < M_Z\) (or vice versus), \(R = \text{Maximum}(R_X, R_Z)\) would be needed for resolution of Y. In table D1 this means that one isobar has a positive \(\Delta M\) and the other a negative \(\Delta M\), and the ‘\(\Delta M\) Ratio’ (based on E11) will be negative. Otherwise, take \(|\Delta M_{XY}| < |\Delta M_{YZ}|\) and let x be the ratio between the two,
Because the curves are Gaussian they fall off rapidly away from the peak, but $R_Z > R_X$ is still possible. Rearrangement of E 9 and elimination of common factors gives,

$$E_{12} \quad \frac{M_Z}{\Delta M_{ZY}} \cdot \sqrt{\ln((u \cdot I_{YZ})^{-1})} > \frac{M_X}{\Delta M_{XY}} \cdot \sqrt{\ln((u \cdot I_{yx})^{-1})} \cdot \left(\frac{M_X}{\Delta M_{XY}} - \frac{M_Z}{\Delta M_{ZY}}\right) \cdot \sqrt{\ln(u^{-1})}$$

If $M_Z < M_X < M_Y$ then $\frac{M_X}{\Delta M_{XY}} - \frac{M_Z}{\Delta M_{ZY}} > 0$. If $M_Y < M_X < M_Z$ then express $M_Z = M_X + \zeta$ and then

$$\Delta M_{ZY} = \Delta M_{XY} + \zeta.$$ Then, $\frac{M_X}{\Delta M_{XY}} - \frac{M_Z}{\Delta M_{ZY}} = \frac{M_X}{\Delta M_{XY}} - \frac{M_X + \zeta}{\Delta M_{XY}} = \frac{\zeta \cdot M_X - \zeta \cdot \Delta M_{XY}}{\Delta M_{XY} \cdot (\Delta M_{XY} + \zeta)} > 0.$

Then, $\frac{M_X}{\Delta M_{XY}} \cdot \sqrt{\ln((u \cdot I_{yx})^{-1})} \cdot \left(\frac{M_X}{\Delta M_{XY}} - \frac{M_Z}{\Delta M_{ZY}}\right) \cdot \sqrt{\ln(u^{-1})} > \frac{M_X}{\Delta M_{XY}} \cdot \sqrt{\ln((u \cdot I_{yx})^{-1})}$. Using this with E12, an approximate limit at which $R_Z > R_X$ may be derived:

$$\frac{M_Z}{\Delta M_{ZY}} \cdot \sqrt{\ln((u \cdot I_{YZ})^{-1})} > \frac{M_X}{\Delta M_{XY}} \cdot \sqrt{\ln((u \cdot I_{yx})^{-1})} \quad \Rightarrow \quad \frac{M_Z}{\Delta M_{ZY}} \cdot \frac{\Delta M_{XY}}{M_X} = \frac{M_Z}{M_X} > \frac{\sqrt{\ln((u \cdot I_{yx})^{-1})}}{\sqrt{\ln((u \cdot I_{YZ})^{-1})}}$$

$$E_{13} \quad \therefore \quad (u \cdot I_{YZ})^y > u \cdot I_{yx}$$

$$E_{14} \quad k = \left(\frac{\Delta M_{XY}}{\Delta M_{ZY}} \cdot \frac{M_Z}{M_X}\right)^2 = \left(\frac{1}{x} + \left(\frac{1-x}{x}\right) \cdot \left(\frac{\Delta M_{XY}}{M_X}\right)^2\right) \quad \text{for (1)}$$

$$\quad \text{for (2)}$$

$$E_{15} \quad \text{with x from E11. Also, since} \quad I_{yz} = \frac{I_y}{I_z} \quad I_{yx} = \frac{I_y}{I_x} = I_{yx} \cdot I_{xz} \quad \text{then E13 may be rewritten as:}$$

$$I_{xz} > (u \cdot I_{yx})^{\left(\frac{1-k}{k}\right)}$$

The relative abundance of X to Z, $I_{xz}$, is now related to the relative abundance of Y to X, $I_{yx}$, with k given by E14. If E13 or E15 are satisfied then $R_Z > R_X$ and $R > R_Z > R_X$ will be needed to resolve the two peaks from Y, otherwise $R_X$ should suffice (assuming Gaussian peaks and background only from peak tails). The following provides another check.
In the limit $x << \left| \frac{M_x}{\Delta M_{xy}} \right|$ (for example $x < 10, \left| \frac{M_x}{\Delta M_{xy}} \right| > 1000$), $k \approx x^{-2}$:

$$k \xrightarrow{x \ll \left| \frac{M_x}{\Delta M_{xy}} \right|} x^{-2}$$

Condition E15 may be approximated in this limit as:

**E 16**

$$I_{XZ} > (u \cdot I_{YX})^{(x^2-1)}$$

Again, $x$ is given by E11. From Figure D1 it is seen that all of the atomic isobars and most of the molecular isobars listed in Table D1 satisfy $\left| \frac{M_x}{\Delta M_{xy}} \right| > 1000$, and E17 provides a quick check to see if $R > R_X$ would be needed for resolution of $Y$. If E17 is true then $R \geq R_Z > R_X$ is needed otherwise $R_X$ will suffice to resolve the isobars from $Y$ (assuming Gaussian peaks and background only from peak tails).

In AMS applications $X$ is typically several orders of magnitude more abundant than $Y$ so that $I_{YX} << 1$. A useful condition is to determine the values of $x$ (E11) such that $R_Z = R_X$ is needed for resolution of $Y$ when the relative abundance of $X$ to $Z$ is the same as that of $Y$ to $X$ (in which case the relative abundance of $Y$ to $Z$ would be $(I_{YX})^2$). That is, the values of $x$ such that $R_Z = R_X = R$ when $I_{XZ} = I_{YX} = I$ for resolution from $Y$. In this case the relative abundance of $X$ to $Z$ would be $I_{XZ} = I_{YX} << 1$ and typically $Z$ would have to be many orders of magnitude more abundant than $X$ in order to require consideration. Either $X$ would have to be a rare isotope, perhaps very short lived, or $Z$ would have to be a much more abundant isotope (eg. $X$ radioactive with intermediate half-life and $Z$ stable). From E15,

$$\ln I > \left( \frac{1-k}{k} \right) (\ln u + \ln I)$$

**E 18**

$$\Rightarrow k > \frac{\ln u + 1}{\ln I + 2} = \frac{\ln u + \ln I}{\ln u + 2 \ln I}$$

When E16 applies (as for all atomic isobars in table D1),

**E 19**

$$x > \sqrt{\frac{\ln u + 2 \ln I}{\ln u + \ln I}} \xrightarrow{\ln I \gg \ln u} \sqrt{2}$$

Some values of E19 are given in Table E2 for $u = 1/6$. For $I \leq 10^{-2}$, $x > 1.3$ and by $I = 10^{-14}$ the $\sqrt{2}$ limit is more or less reached. In general, if $X$ is at least 10 times more abundant than $Y$ and $| \Delta M_{ZY} | > 1.4 | \Delta M_{XY} |$ then $Z$ will generally have to be several orders of magnitude more
abundant than X before $R_X$ is insufficient to resolve $Y$ from $Z$ if all curves are Gaussian and backgrounds are only due to curve tails. Only 4 isobar pairs satisfy $|\Delta M_{ZY}| \leq 1.4|\Delta M_{XY}|$ in table D1.

Figure E3 is a plot of $I_{yx} = (I_{xy})^{-1}$ versus $|\Delta M_{ZY}/\Delta M_{XY}|$ for several values of $I_{xy} = (I_{yx})^{-1}$ (inverses are used so that positive exponents are plotted) using E15 and E19, and $M_X/\Delta M_{XY} = 1000$ is used so that the limit of E16 would apply to cases in table D1 and the curves would apply to larger values of $M_X/\Delta M_{XY}$. It is clear that for $|\Delta M_{ZY}| \geq 1.5|\Delta M_{XY}|$, $Z$ would have to be at least 1 order of magnitude more abundant than $X$ in order for it to contribute to the background if curves were Gaussian and background were only due to peak tails.

**E.VI Summary Example Using $^{36}$Cl**

For this section, $Y = ^{36}$Cl and the isobars to be considered are $^{36}$S, $^{36}$Ar, $^{18}$O$_2$ and $^{12}$C$_3$, with $\Delta M$ and $M/\Delta M$ values as listed in table D1. If all isobars were present then $R \geq R_{^{36}Ar}$ would be needed to resolve $^{36}$Cl at 3 times the background assuming all peaks were Gaussian and all background were due to peak tails. Suppose all isobars were equally abundant except $^{36}$Cl which will be assumed 8 orders of magnitude less abundant ($I_{yx} = 10^{-8}$ for all isobars). Then $R_{^{36}Ar} \geq 3.5 \times 47300 = 165550$ (at FWHM, tables D1 and E1). Only for $^{36}$Ar and $^{36}$S is $\Delta M > 10^4$, however since $|\Delta M_{^{36}Ar}/\Delta M_{^{36}S}| = 1.6$ (table D1), from figure E3, $^{36}$S would have to be 11 orders of magnitude more abundant than $^{36}$Ar for this resolving power to be insufficient, which is not the assumed case.

The situation is shown in figure E4 where the $^{36}$Cl peak is indeed resolved with $R_{^{36}Ar}$. If anions were used then $^{36}$S/$^{36}$Ar $< 10^{-11}$ for most systems (metastable Ar$^-$ exists, $\tau = 260 \pm 25$ ms, Ben-Itzhak et al. 1988) and $R_{^{36}S} = 102900$ (tables E1 and D1) would be sufficient. Under these conditions and with sufficient dynamic range, to go to $^{36}$Cl/$^{36}$S $= 10^{-16}$ would require 1.3 times the resolving power (table E1), $R = 133770$. If both $^{36}$S and $^{36}$Ar could be suppressed to one order of magnitude below the $^{36}$Cl abundance, then resolution to $10^{-16}$ from the other two isobars considered would only require $R = 5500$ (tables E1 and D1), 4% of $R_{^{36}S}$. 
Figure E 3: Relative Abundance Limits for Z to Contribute Substantially to the Background of Y if a Closer Isobar X were already resolved

Equation E15 is used to plot the minimum required relative abundance of Z to X, $I_{ZX} / I_X = I_{XY}^{-1}$, before $R_X$ is insufficient to resolve Y from Z (assuming all curves are Gaussian) for 8 values of $I_{XY}$. In general, Z must be many orders of magnitude more abundant than X for $R_X$ to be insufficient. The dashed line is a plot of E19, the point at which $I_{ZX} = I_{XY}$ so that $I_{YZ} = (I_{XY})^2$.

Table E 2: Tabulated Values from E19 with $u = 1/6$

<table>
<thead>
<tr>
<th>$I$</th>
<th>0.5</th>
<th>0.1</th>
<th>$10^{-2}$</th>
<th>$10^{-3}$</th>
<th>$10^{-4}$</th>
<th>$10^{-5}$</th>
<th>$10^{-6}$</th>
<th>$10^{-9}$</th>
<th>$10^{-14}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$</td>
<td>1.14</td>
<td>1.25</td>
<td>1.31</td>
<td>1.34</td>
<td>1.36</td>
<td>1.37</td>
<td>1.38</td>
<td>1.39</td>
<td>1.40</td>
</tr>
</tbody>
</table>
This is a mock $^{36}$Cl mass spectrum with resolving power $R_{\text{FWHM}} = 475500$, based on $M/\Delta M$ for $^{36}$Ar and $^{36}$Cl (table D1) and E9 / table E1, for neutral isobars. Masses given are based on $^{36}$S and $^{36}$Ar (Baum et al. 2002), and calculations (see Appendix D and table D1). The curves are plotted according to E10 with $H_0 = 1$ for all except $^{36}$Cl ($H_0^{\text{Cl}} = 10^{-8}$). Solid lines represent the sum of all curves, dashed lines represent individual curves and dot-dashed lines indicate a region of magnification. At this $R_{\text{FWHM}}$ the $^{36}$Cl peak is resolved at 3 times the background.
APPENDIX F

36Cl Nuclear Properties and Mass

The mass of 36Cl is generally not published in typical data sources, including the ones referenced in this thesis (eg. Baum et al. 2002, Haynes and Lide 2011, Firestone and Shirley 1996, NIST 2011). It is calculable as described in Appendix D, however, based on the energetics of its decay and properties of the daughter products 36Ar and 36S.

F.I Summary

Table F 1: Calculated Quantities for 36Cl Based on Decay Series

<table>
<thead>
<tr>
<th>Calculated 36Cl mass</th>
<th>35.9683070 amu</th>
</tr>
</thead>
<tbody>
<tr>
<td>36Cl and 36S mass difference</td>
<td>$\Delta M_{36ClS} = 0.0012261 \text{amu} = 1.14207 \text{MeV} \approx 2.2m_e$</td>
</tr>
<tr>
<td>36Cl and 36Ar mass difference</td>
<td>$\Delta M_{36ClAr} = 0.0007607 \text{amu} = 0.7086 \text{MeV} \approx 1.4m_e$</td>
</tr>
</tbody>
</table>

Figure F 1: 36Cl Decay Diagram

Symbols: $\varepsilon c$ orbital electron capture; $\beta^+/\beta^-$ beta decay; $^{\text{12}}X$ element X with total number of nucleons A, number of protons Z, number of neutrons $N_p = A - Z$; †Q is actual mass difference between neutral atoms; †,‡$T_{1/2}$ half life; †,‡% S or Ar is natural abundance, †m mass based on $^{12}\text{C} = 12$ amu; ‡E is $\beta^+$ kinetic energy; ‡branching % $\varepsilon c + \beta^+$ and $\beta^-$; ‡branching % $\beta^+$.

†: Firestone and Shirley (1996 p. 113 – 118); ‡: Baum et al. (2002 p. 44 – 45).
F.II  Nuclear Properties and Transmutation Dynamics of $^{36}$Cl

The only radioactive isotope of Cl with $\tau_{1/2} > 1$ hr is $^{36}$Cl which has an even number of nucleons, $A = 36$, but odd numbers of protons, $Z = 17$, and neutrons, $N_n = A - Z = 19$. The decay channels are shown in figure C1, and the following uses the symbols defined therein.

In terms of the nuclear shell model, let $1 \leq r \leq l$ represent the shell, $l = r - 1$ represent the angular momentum associated with an orbital in shell $r$, $s$ represent the spin of a nucleon ($s = 1/2$ for protons and neutrons), $j = l + s$ represent the spin-orbit coupling angular momentum of a nucleon, and $J = \left( \sum_{p=1}^{L} j_p + \sum_{n=1}^{L-2} j_n \right)$ represent the total nuclear angular momentum. Neutron and proton shells may be considered to fill independently and subscripts $n$ and $p$ will be used for neutrons and protons respectively.

Each shell orbital is occupied by $2j + 1$ nucleons and each shell has $l$ orbitals. Then, there are $2j + 1 = 2$ nucleons in a filled $r = 1$, $2j + 1 = 4$ ($l=1$) + $2j + 1 = 2$ ($l = 0$) = 6 nucleons in a filled $r = 2$, 12 nucleons in a filled $r = 3$ and so on. An atom with the $r = 2$ proton and neutron shells filled would have a total of 2 ($r=1$) + 6 ($r=2$) = 8 neutrons and 8 protons, and so the nucleus would have a total of 16 nucleons, which is $^{16}$O. In a nuclear ground state, one may consider the shells $r$ to fill from higher $l$ value orbital to lower.

Applied to $^{36}$Cl in the ground state, $N_n = 19$ and the neutron shells are filled as $N_n(r=1) = 2, N_n(r=2) = 6, N_n(r=3) = 11$. That means that there is one un-paired neutron in the $l = 0$ orbital in the $r = 3$ shell. For this neutron, $j = 1/2$ and $J = 1/2$ since all the other neutrons are spin-paired. On the other hand $Z = 17$ and the proton $r = 3$ shell has three vacancies: the $l = 0$ orbital is completely empty and the $l = 1$ orbital has an unpaired proton with $j = 3/2$. That means $J_p = 3/2$ since all other protons are spin-paired. Then, $J = 2$ for $^{36}$Cl.

It is then perhaps not too surprising that that $^{36}$Cl has a large neutron capture cross section and transmutes by both $\beta^-$ and $\beta^+$ decays and through $\epsilon c$ (see Figure F 1: $^{36}$Cl Decay Diagram). In all cases, the ground-state daughter products have no spin-unpaired nucleons ($J = 0$) and they either have all populated orbitals filled or have one shell completely filled.

By $\beta^-$ decay, a neutron in the $^{36}$Cl nucleus is replaced with a proton (see Appendix C) and a stable $^{36}$Ar atom is produced. In the $^{36}$Ar ground state, both neutron and proton $r = 1, 2$
shells are filled, two of the three \( r = 3 \) orbitals are filled and the \( r = 3, l = 0 \) neutron and proton orbitals are both empty. All of the protons and neutrons are spin-paired; \( J_n = J_p = J = 0 \).

Conversely, through \( \beta^+ \) decay and \( \varepsilon c \), a neutron is replaced with a proton (see Appendix D) and a stable \( ^{36}S \) is produced. In the \( ^{36}S \) ground state, \( N_p = 20 = \) ‘magic number’ meaning that all of the neutron orbitals of the populated shells are all completely empty. All of the protons are also spin-paired although the \( r = 3 \) shell, \( l = 0 \) orbital is completely empty; \( J_n = J_p = J = 0 \).

**F.III Calculation of \( ^{36}Cl \) mass and Stable Atomic Isobar \( \Delta M \)**

The Q-values of Figure F 1 give the mass difference between \( ^{36}Cl \) and its daughter products, where \( ^{36}Cl \) must be the more massive nuclide of the three and by the Q-values it is seen that \( M_{^{36}Cl} > M_{^{36}Ar} > M_{^{36}S} \) (see Appendix D). Using Figure F 1,

\[
\Delta M_{^{36}ClS} = (M_{^{36}Cl} - M_{^{36}S}) = Q = 1.14207 MeV > 2m_e
\]

\[
\Delta M_{^{36}ClAr} = (M_{^{36}Cl} - M_{^{36}Ar}) = Q = 0.7086 MeV < 2m_e
\]

It is clear that these are very close isobars, the mass difference between \( ^{36}Ar \) and \( ^{36}Cl \) is less than two electron masses while that between \( ^{36}Cl \) and \( ^{36}S \) is just over \( 2m_e \). Using Table A2,

\[
\Delta M[amu] = \frac{10^{-9} c^2}{N_e} \cdot Q \left[ \text{amu} \cdot MeV \right]
\]

This gives the difference in mass between the isobars \( ^{36}Cl, ^{36}S \) and \( ^{36}Ar \). Then, the mass of \( ^{36}Cl \) is:

\[
M_{^{36}Cl}[amu] = \frac{N_e}{10^{-9} c^2} \cdot 1.14207 + M_{^{36}S} = 0.0012261 + 35.9670809 = 35.9683070 \text{amu}
\]

\[
M_{^{36}Cl}[amu] = \frac{N_e}{10^{-9} c^2} \cdot 0.7086 + M_{^{36}Ar} = 0.0007607 + 35.9675463 = 35.9683070 \text{amu}
\]

\[
\Delta M_{^{36}ClS} = 0.0012261 \text{amu}
\]

\[
\Delta M_{^{36}ClAr} = 0.0007607 \text{amu}
\]

Values have been rounded according to the significant figures of the experimentally measured Q values and masses of \( ^{36}S \) and \( ^{36}Ar \). On a final note, \( \Delta M_{^{36}SAr} \) may be calculated without knowing either of their masses through their decay Q-values, \( \Delta M_{^{36}SAr} = (1.14207 - 0.7084) \text{ MeV} < m_e \), and since Q is less for the \( ^{36}Ar \) transition, \( M_{^{36}Ar} > M_{^{36}S} \).
APPENDIX G

$a_2 - q_2$ Stability Diagrams and RF Heating Coefficients

Figure G 1: General $a_2 - q_2$ Quadrupole Stability Diagram

Figure 2. The stability diagram for the two-dimensional case where the $x$ and $y$ directions differ by a factor of $-1$. Detail of the first stability region is given in Fig. 10.

Reprinted from Dawson (1986, figure 2 on p. 4) with permission from John Wiley and Sons © 1986.
Figure G 2: First $a_2 - q_2$ Quadrupole Stability Region

Fig. 10. Stability diagram for an infinitely long and perfect quadrupole in the dimensionless space of $(a, q)$, where $a$ and $q$ are the Mathieu parameters given by Eqs. (3.5) and (3.6) in the text. Ions that are within the enclosed region are considered to be stable, while ions that are outside of this region are considered to be unstable. Also shown are the iso-beta lines that can be used in calculating the frequencies of ion oscillation in the quadrupole.

Reprinted from Tanner et al. (2002, figure 10 on p. 1393) with permission from Elsevier © 2002.
Figure G 3: Second $a_2 - q_2$ Quadrupole Stability Region

Figure 1. The second stability region in the Mathieu parameter $a-q$ plane. The dashed lines are iso-$\beta$ lines for motion in the $x$ and $y$ directions. The solid lines are resonance lines giving maximum transmission for $n = 10$. Points along the scan line $a = 2\lambda q$ correspond to maximum transmission where strong focusing takes place in the $x$ and $y$ directions simultaneously.

Reprinted from Du et al. (1999, figure 1 on p. 1264) with permission from Elsevier © 1999.
Table G.1: RF Heating Coefficients for use with Eq 4.42.

These coefficients are used for calculating RF heating contributions according to Eq 4.42. Reprinted from Baranov et al. (2005, table 1 on p. 41) with permission from Elsevier © 2005.

<table>
<thead>
<tr>
<th>(b \cdot a)</th>
<th>(b/a \cdot \xi_{\text{e}})</th>
<th>(b/a \cdot \xi_{\text{n}})</th>
<th>(b/a \cdot \xi_{\text{e}})</th>
<th>(b/a \cdot \xi_{\text{n}})</th>
<th>(b/a \cdot \xi_{\text{e}})</th>
<th>(b/a \cdot \xi_{\text{n}})</th>
<th>(b/a \cdot \xi_{\text{e}})</th>
<th>(b/a \cdot \xi_{\text{n}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.02</td>
<td>0.03</td>
<td>-0.2</td>
<td>-0.07</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>0.5</td>
<td>0.05</td>
<td>0.05</td>
<td>-0.1</td>
<td>-0.1</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>1.0</td>
<td>0.10</td>
<td>0.10</td>
<td>-0.1</td>
<td>-0.1</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2.0</td>
<td>0.20</td>
<td>0.20</td>
<td>-0.1</td>
<td>-0.1</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>4.0</td>
<td>0.40</td>
<td>0.40</td>
<td>-0.1</td>
<td>-0.1</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>8.0</td>
<td>0.80</td>
<td>0.80</td>
<td>-0.1</td>
<td>-0.1</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>16.0</td>
<td>1.60</td>
<td>1.60</td>
<td>-0.1</td>
<td>-0.1</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Values of \(\xi_{\text{e}}\) and \(\xi_{\text{n}}\) for selected \(a\) and \(\xi_{\text{e}}\) parameters.
Initially an attempt was made to upload this thesis to the University of Toronto electronic repository as a ‘PDF’ file on March 14\textsuperscript{th}, 2012, at 16h00 (3 – 14 – 16). Unfortunately some problems occurred during conversion to PDF and the upload had to wait until March 15. March 14\textsuperscript{th} is known to some as π-day for the irrational number. I share a poem given to me by a friend, John of Amnesia on Bloor Street (please forgive the Greek spelling, it had been a while since this poem was recalled and there may be some mistakes),

\begin{quote}
Αεί, ὁ Θεός ὁ μέγας γεωμετρεῖ αν φτιαξῇ ριθόν απεραντὸν ωρισεν τὸν τοὺς
\end{quote}

– Saints, (the) God the great contemplating to form so he can create a number boundless he defined this.

Count the letters in each word of the Greek version of the poem (save for the last ~ 3 words). Write them in sequence, adding a decimal (.) where the comma (,) appears (in accordance with British numerical formatting). Finally, compare the real number representation of the irrational number π with that sequence.