DIRECT MEASUREMENTS OF LINE MIXING, LINE BROADENING, 
AND TRANSLATIONAL LINE SHAPE 
IN THE 
v_{1}+v_{2} Q-BRANCH OF PURE CO_{2} 

by 

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ABSTRACT

DIRECT MEASUREMENTS OF LINE MIXING, LINE BROADENING, AND TRANSLATIONAL LINE SHAPE IN THE $v_1+v_2$ $Q$-BRANCH OF PURE CO$_2$

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An infrared difference frequency spectrometer was improved such that the baseline spectra were constant to within 1 part in 1000 over a 1.3cm$^{-1}$ scan. Over a 0.5 second integration time, transmission through the gas cell could be measured with a frequency resolution of 1.5MHz and a signal-to-noise ratio in excess of 2000:1. Using this spectrometer, line mixing and high resolution line shape effects have been directly measured for the $v_1+v_2$ band of CO$_2$.

At pressures lower than 11kPa, the spectra were analysed within the Rosenkranz line mixing approximation. Translational effects were encompassed using the hard collision model of Nelkin and Ghatak (1964), modified to include an asymmetry component due to line mixing. For each line between $Q(2)$ and $Q(30)$, the Rosenkranz first order line mixing coefficients, broadening coefficients, and narrowing parameters were measured. The line mixing coefficients were found to be qualitatively consistent with, but significantly different from, the mixing coefficients calculated by Strow et al. (1994) using an Exponential Power Gap (EPG) law. The broadening coefficients, estimated to be accurate to within 0.5% on average, were found to be consistent with the $P$- and $R$- branch broadening measurements made by other groups. The narrowing parameters were found to be strongly non-linear with pressure, a symptom of speed-dependent line shape effects unaccounted for by the line shape model used.

In addition to the line parameters, the band shift and band strength were measured to 5% and
0.5% accuracy respectively. No other shift measurements of this band have been reported for comparison. However, the band strength was found to be 3% lower than the currently used value of Hitran96 and 2% higher than other recent measurements of this band.

To analyse spectra at pressures greater than 11kPa, an empirical speed-dependent profile was formed from the sum of two hard collision profiles. Only with this profile could spectra up to 72kPa be fitted within error. The spectra displayed strong non-linear line mixing effects. In particular, intensity transfer between lines was directly measured and found to agree qualitatively with that predicted by an EPG scaling law calculation.
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CHAPTER 1

INTRODUCTION

1.1 OVERVIEW

It has long been known that gases absorb and emit radiation at certain characteristic frequencies which correspond to transitions between energy levels of the molecule. Traditional gas phase spectroscopy is predominantly concerned with measuring and calculating these transition frequencies, and to a lesser extent the determination of intensities. Over time, with improved measurements and understanding, it was realised that these transitions do not occur at precise frequencies, but rather the molecules absorb and emit over some frequency range centred around a transition frequency. The emission or absorption as a function of frequency is known as the line shape and is the subject of this thesis.

In the past few decades spectroscopic studies have led to a more fundamental understanding of atomic and molecular structure. Spectroscopy has also found applications in remote sensing. Two common examples are the remote sensing of planetary atmospheres from satellites and the measurement of combustion processes within a combustion chamber.

As far back as the 1800's, spectroscopy was used for remote sensing of the Sun's composition. Unidentified lines in the solar spectrum led to the discovery that the Sun is composed largely of helium. Just as those early experiments taught us about the Sun, spectroscopy can teach

\[\text{We will exclusively refer to molecules in this thesis although much of what is said could also apply to atoms.}\]

\[\text{We define remote sensing to be the measurement, from a distance, of a system's characteristics using its radiative properties.}\]
us about our own atmosphere. Concerns about the environmental changes that are occurring on our planet have fuelled a flurry of research aimed at studying the Earth’s atmosphere. Line shapes are crucial elements both to our understanding of the Earth’s atmospheric radiative properties and in our ability to make remote sensing measurements of its condition. With the need for more detailed understanding and more precise remote sensing methods, the importance of having accurate line shape models has become apparent. This is particularly true for gases such as carbon dioxide (CO$_2$) and water vapour which play a major role in the “greenhouse effect”, a key component of the Earth’s climate system (Houghton et al., 1996).

Carbon dioxide is the molecule of choice for satellite remote sensing of atmospheric temperature profiles of the Earth’s atmosphere. Important in their own right, temperature profiles are also ancillary information required for remote sensing of other trace gas constituents. There are two principal reasons for choosing CO$_2$. The atmospheric mixing ratio of CO$_2$ is nearly constant at altitudes less than 80km and hence there is one less unknown when interpreting the remote sensing measurements of CO$_2$ versus other less uniformly distributed gases. The second reason is that CO$_2$ is a dominant infrared absorber in the upper atmosphere which allows measurements of temperature up to 80km in altitude (Taylor et al., 1972).

Line shapes are known to depend on the molecular species, the temperature and pressure of the sample, and the presence of other gases, known as buffer gases. Since these conditions are far from homogeneous in the atmosphere, the line shape for a given molecule will vary depending on its surroundings. Atmospheric pressure decreases approximately exponentially with height from around 100kPa at ground level to zero at infinite altitude. Temperature varies not only with seasonal fluctuations but also with altitude. For example, in the tropics, temperatures at altitudes of 20km can drop to 200K, although the temperature at ground level is over 300K.

The most abundant constituents of the lower atmosphere, nitrogen and oxygen, are of nearly uniform concentration below 80km. Being infrared inactive, their role is limited to being perturbers of spectral lines. However, some minor constituents, such as water and ozone, vary dramatically in concentration.
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Figure 1.1. Measured transmission spectra of pure CO₂. a) Low pressure spectrum, measured using a Fourier transform infrared spectrometer (courtesy A. Predoi-Cross), showing the P-, Q-, and R-branches of the v₁+v₂ band we studied. b) The Q-branch spectrum at 6.6kPa, measured with the high resolution difference frequency spectrometer. Note that the detailed structure of the Q-branch occurs over a very small frequency range.

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An even greater variety of conditions is found on other planets such as Mars and Venus. The Venusian atmosphere is composed of more than 90% CO\textsubscript{2} and has a surface pressure and temperature of 9 MPa and 750K respectively. The Martian atmosphere is composed of more than 80% CO\textsubscript{2}, with a surface pressure and temperature of 700Pa and 240K.

These diverse environments preclude the possibility of making experimental line shape measurements under all possible conditions. What is practical and necessary, is an understanding of the mechanisms which would allow us to calculate or model line shapes under a variety of conditions and with a minimum of experimentally determined parameters.

A topic of current research is the effects which govern the shapes of lines belonging to spectral regions referred to as $Q$-branches.\textsuperscript{3} The dominant feature of lines belonging to a $Q$-branch is that they tend to be closely spaced in frequency. It is the tight spacing of lines that not only makes $Q$-branches of interest for remote sensing applications but also makes them so difficult to study. Figure 1.1 shows a broad region of the CO\textsubscript{2} spectrum taken by a Fourier transform spectrometer and an experimental spectrum taken for this thesis. The $Q$-branch spectrum shows the detail that exists within such a small part of the total spectrum.

As an example of the difficulty of measuring line parameters for a $Q$-branch, consider one of the most basic line shape parameters, the pressure broadening coefficient, which determines the linear rate at which the line width increases with pressure. Typically, measurements of broadening coefficients are performed on lines which are well separated. Since the closely spaced lines of a $Q$-branch overlap significantly at all but the lowest pressures, measurement of the broadening coefficients is very difficult. In the case of $Q$-branch lines of CO\textsubscript{2}, only a handful of broadening coefficients have ever been measured (Gentry and Strow, 1987). When $Q$-branch line widths are required, the practice has been to assume that the line widths are branch independent. The $Q$-branch line widths are then set equal to the measured widths of lines belonging to other branches where the lines are less closely spaced (Rothman \textit{et al.}, 1992b). There has been little experimental evidence to

\textsuperscript{3}A spectroscopic branch is a set of transitions grouped according to the means by which the molecule undergoes internal energy change. $Q$-branch transitions are defined to be those in which the molecule changes its vibrational energy state, but not its rotational energy state.
justify this assumption (Strow and Pine, 1988; Pine and Looney 1992).

As the broadening coefficient example illustrates, the measurement of individual line parameters is made difficult by the overlapping nature of $Q$-branch lines. But, the problem is more difficult yet. The traditional picture treats the individual lines as isolated (although overlapped), independent transitions. In that case the shape of the $Q$-branch can be formed by summing the individual line shapes. Although this isolated line approach is simple, and for many situations sufficiently accurate, it is a poor approximation for $Q$-branches. For $Q$-branch lines we must also address the interdependence of lines. The term "line mixing" refers to the line shape effects which result from this interdependence or interference of lines (Levy et al., 1992). Line mixing is particularly important for $Q$-branches because, in general, the closer two interfering lines are, the stronger the line mixing.

The impact of line mixing on temperature retrievals from satellites has been discussed by several authors. In each case they included an estimate of line mixing effects in a retrieval algorithm. In the cases discussed below, results from calculations which included line mixing were compared to those using an isolated line shape.

Strow and Reuter (1988) investigated potential errors in the retrievals of upper atmospheric temperature measured from satellite nadir views. (A nadir view is a nearly vertical view through the earth’s atmosphere.) Their analysis looked at the $v_2$ fundamental band of CO$_2$ at 15μm (667 cm$^{-1}$) which, because it is a strong band, is most sensitive for satellite measurements of temperature in the higher parts of the atmosphere (Taylor et al., 1972). They estimated that the potential error caused by ignoring line mixing in the retrieval algorithm could be as large as 3K.

Edwards and Strow (1991) did a similar investigation for the Upper Atmospheric Research Satellite (UARS) which was equipped with limb scanning instruments (limb scanning satellites look through the atmosphere tangent to the earth’s surface). In particular they looked at the Improved Stratospheric And Mesospheric Sounder (ISAMS) and the Cryogenic Limb Array Etalon Spectrometer (CLAES) instruments on board UARS. The ISAMS and CLAES instruments were designed to look at the 617 cm$^{-1}$ and 791 cm$^{-1}$ CO$_2$ bands respectively. Both of these instruments were designed to measure temperature to 1K accuracy. The bands used are weaker than the $v_2$ CO$_2$ band
studied by Strow and Reuter, and thus more sensitive to the lower altitude (higher pressure) regions of the atmosphere. Edwards and Strow found that the brightness temperature retrieved from ISAMS was relatively insensitive to line mixing but could be in error by up to 2 K if it was completely ignored. The equivalent brightness temperature from the CLAES instrument was more sensitive to line mixing and failing to take it into account could cause errors as large as 10 K. Unfortunately, the eruption of Mount Pinatubo created large uncertainties in the UARS temperature retrievals which prevented line mixing effects from being investigated experimentally during that mission (Edwards, 1997).

Observational evidence of line mixing in a remote sensing application was presented by Rinsland and Strow (1989). They analysed spectra taken with the Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument. Measured absorption coefficients for the CO$_2$ Q-branch at 1932 cm$^{-1}$ were 0.62 times what was predicted with line mixing ignored. The measurements were made over a range of heights between 13 and 22 km at temperatures of approximately 210 K. They concluded that these differences were significant even at pressures as low as 10 kPa. Including an estimate of line mixing gave a maximum disagreement with observed spectra of approximately 10% in absorption coefficient.

Although, as we shall see, much of the theory behind line mixing is already understood, quantifying the effect has proven to be a difficult task. Each line within the Q-branch interferes with all other lines within the branch\textsuperscript{4}. The set of interactions for all pairs of lines can be collected into a single, generally complex matrix, called the relaxation matrix. Herein lies the difficulty in quantifying line mixing: whereas other line shape effects usually require only a single parameter per line, line mixing requires an entire matrix of parameters.

At present, direct measurement of a relaxation matrix for any gas has only been accomplished in a few special cases in which there were only a small number of strongly interacting lines (Sinclair \textit{et al.}, 1993). Most research is aimed at indirectly determining the relaxation matrix using computational methods best described as estimators. Typically, the relaxation matrix is estimated from isolated line parameters and a semi-empirical equation referred to as an \textquotedblleft energy gap law\textquotedblright.

\textsuperscript{4}Interference between lines belonging to different branches is also possible but in general it is a much weaker effect.
"scaling law". The branch shape predicted by the estimated relaxation matrix is then compared to experimental spectra over a range of conditions.

This approach is practical in that it can be applied with present experimental parameters, however, it does suffer from several shortcomings. Typically the spectra calculated using a gap law, differ from measured spectra by a few percent (Strow and Gentry, 1986; Rinsland and Strow, 1989; Pine and Looney, 1992). From a practical point of view the agreement is quite remarkable. However, from a more fundamental view point, the discrepancy between theory and experiment is significant in that it suggests a lack of complete understanding of line mixing. It also raises questions about applying these methods to other spectral regions for which there are no experimental spectra for comparison. Unfortunately, with the approach outlined in the previous paragraph it is difficult to identify the source of the discrepancy. Is the discrepancy the result of an inaccurate relaxation matrix, or an incomplete line shape model? If the problem is with the relaxation matrix, is it due to errors in the estimation methods used, or errors in the isolated line parameters on which the estimation is based? Previous work on CO$_2$ has not determined the nature of the discrepancy.

This work takes a distinctly different approach: the goal is to make direct measurements of line mixing effects using high quality, experimentally obtained spectra. With experimental spectra of sufficient frequency resolution and signal-to-noise ratio, $Q$-branch spectra with individually resolved lines are analysed and deviations from the isolated line shape model are measured. The observed line mixing effects are then quantified on a line-by-line basis. At higher pressures, lines overlap more severely and are no longer individually resolved. Under these conditions the line mixing effects become quite large, although more difficult to quantify. We will show that with our high quality spectra even higher pressure line mixing effects can be analysed.

In the 2.3-5.5μm (1800-4300cm$^{-1}$) range of our instrument, we measured the strong 4.8μm (2077cm$^{-1}$) CO$_2$ $Q$-branch since it suffered from minimal overlap with adjacent bands. This band is also representative of the 15μm bending bands which are of immediate interest to the atmospheric community (Strow and Gentry, 1986). Spectra of pure CO$_2$ were used so that the absorption cross section was sufficiently large that spectra could be taken using a simple, one metre, single pass gas cell.
In the course of this study we needed to address several line shape mechanisms other than line mixing. There were two fundamental reasons for their inclusion. Firstly, the success of fitting spectra within experimental error estimates would implicitly verify our line mixing, line shape model. However, fits within error would not be possible unless other important line shape effects were also included. Secondly, the nature of any fitting algorithm allows errors in line shape to couple into the measurements of line mixing effects. Therefore, as a by-product of these fits, other isolated line shape parameters have been measured, including the aforementioned \( Q \)-branch pressure broadening coefficients.

Fitting spectra within the limits of experimental error is only one half of the task. The results must also be physical. Each parameter has an expected behaviour with pressure. All the parameters determined from the fits were compared to existing theories and measurements. In particular, the line mixing measurements were compared to predictions based on a simple gap law estimate of the relaxation matrix (Strow et al., 1994).

The results presented in this thesis were made possible by the high quality of the spectra obtained using the experimental apparatus. The infrared spectrometer we used generated infrared radiation using difference frequency technology. The resolution of the spectrometer, limited only by the line width of the visible lasers, was approximately 1.5MHz \((5 \times 10^5 \text{cm}^{-1})\) and the signal-to-noise ratio was estimated to be in excess of 2000:1. At present there is no other spectroscopic technique which can achieve equivalent performance.

1.2 Thesis Outline

In the Theory chapter we will review and develop the line shape mechanisms used for the analysis of the spectra. Chapter 3, Background, will contain a short review of the background literature that pertains to the study of line mixing, particularly in \( \text{CO}_2 \) \( Q \)-branches.

The experimental methods and the difference frequency spectrometer will be described in detail in the Experimental chapter. This chapter will describe the theory behind difference frequency generation and how it was implemented in our system. It also contains a review of the improvements
made to the instrument during my research.

Chapter 5, entitled *First Order Line Mixing*, presents the analyses of spectra at pressures under 11kPa using a first order approximation. The following chapter, *Speed-dependent Profile*, contains further line shape theory which was developed to fit the spectra presented in chapter 7, *Higher Order Line Mixing*. In chapter 7 we examine higher order mixing effects as observed in higher pressure spectra.

The final two chapters are entitled *Summary and Conclusions* and *Future Work and Suggestions*.

### 1.3 PERSONAL CONTRIBUTION

The difference frequency system existed at the time I started this research and was the result of a huge effort by Peter Sinclair and Jon Forsman (Forsman *et al.*, 1991) who developed the visible laser apparatus, acquisition software, and frequency measuring hardware, and Philip Duggan (Duggan *et al.*, 1993) who developed the difference frequency technology. It was however improved to its current performance level during the course of my research. During that time, I have changed virtually every element of the infrared optics and made changes to the acquisition software. I also designed the temperature stabilised gas cell and gas handling system used for the measurements.

I have personally made two contributions to the line shape model used. Firstly, I extended the existing hard collision line shape model of Rautian and Sobel’man (1967) to include line mixing effects. Secondly, I formed an empirically based line shape model which efficiently accounted for the dominant effects of a line shape mechanism known as speed dependence.

I wrote all the software that was used for the analysis of the spectra, and finally, I performed all the experiments to acquire the spectra and performed all the analysis of these spectra.
CHAPTER 2

THEORY

2.1 SPECTROSCOPY

It is the energy level structure and symmetry properties of a molecule which determine its transition frequencies. For the line shape analysis of an isolated line one can virtually ignore the energy level structure of the band to which the line belongs. However, if the lines interact (i.e. mix) then the energy level structure becomes significant. Most of the spectroscopic theory presented here can be found in either the classic reference *Infrared and Raman Spectra* (Herzberg, 1945) or the book *Spectra of Atoms and Molecules* (Bernath, 1995).

The absorption of radiation by a gas involves the transition of a molecule from a lower to a higher internal energy state. Two forms of internal energy relevant to our study are vibrational and rotational energy, each form consisting of quantized levels. The vibrational energy is associated with the motion of atoms within the molecule relative to each other. The energy levels for a given vibrational mode are to first order given by $E_{vib} = (v + \frac{1}{2})\nu_{vib}$, where $v$ is the vibrational quantum number (0, 1, 2, ...) and $\nu_{vib}$ is the vibrational energy spacing. The molecule also rotates about its centre of mass and thus has rotational energy. For linear molecules the rotational energy levels are given to first order by $E_{rot} = B_v J(J+1)$, where $J$ is the rotational quantum number (0, 1, 2, ...) and $B_v$ is the rotational constant for vibrational level $v$. Typically the rotational constant is much smaller than the vibrational constant. For CO$_2$, a mean value of $B_v$ is 0.390cm$^{-1}$, whereas the lowest vibrational frequency is 667cm$^{-1}$.

The following discussion applies to the most abundant isotope of carbon dioxide, $^{12}$C$^{16}$O$_2$. 

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Other isotopes can have a different symmetry. Figure 2.1 shows the three fundamental vibrational bands of the carbon dioxide molecule: $v_1$, the symmetric stretch mode; $v_2$, the bending mode; and $v_3$, the asymmetrical stretch mode. The vibrational transition energies of these modes are 1388.3 cm$^{-1}$ (7.2 μm), 667.3 cm$^{-1}$ (15 μm), and 2349.3 cm$^{-1}$ (4.3 μm) respectively. To interact strongly with infrared radiation, a molecule must have a dipole moment. Carbon dioxide does not have a permanent dipole moment since it is a symmetric linear molecule, but because the bending and asymmetrical stretch modes destroy the linear symmetry, these modes have a time-dependent dipole. The $v_1+v_2$ band we study is a combination band of the symmetric stretch and bending modes.

Infrared transitions are associated with a change in the vibrational quantum level, $v$. With each vibrational level change the associated rotational level change is governed by selection rules. The selection rules are derived on the basis of CO$ _2 $ being a linear symmetric molecule, i.e. with D$_{\infty h}$ symmetry (Bernath, 1995). Because the $v_2$ band is a bending mode, $v_1+v_2$ is classified as a perpendicular band which means that the vibrational mode is perpendicular to the symmetry axis of the molecule. Perpendicular bands have the selection rules $\Delta J=-1,0,+1$, corresponding to $P$, $Q$ and $R$ branches respectively. Bands such as the $v_3$ band are parallel bands which have only $P$ and $R$
Chapter 2: THEORY - Line Shape Theory

branches. The fact that the $Q$-branch lines are separated at all results from the interaction between vibrational and rotational motion of the molecule. To first order, the frequency difference between $Q$-branch vibrotational transitions is given by,

$$\Delta v = \Delta B_{ij} J(J+1)$$

where $\Delta B_{ij}$ is the difference between rotational constants for vibrational levels $i$ and $j$. Because the rotational constant differs little between vibrational levels of CO$_2$, the $Q$-branch lines are generally very closely spaced. For the $v_1+v_2$ band we study, $\Delta B_v = 1.9073 \times 10^4$ cm$^{-1}$. For a further discussion beyond first order see to Rothman et al. (1992b).

The $v_1+v_2$ band has only even $Q$-branch transitions $Q(2), Q(4), ... Q(n)$ with the $Q(0)$ line missing. The absence of the $Q(0)$ line and all odd transitions can be understood on the basis of missing energy levels from either the upper or lower energy state. The ground vibrational level has only even rotational levels because of nuclear symmetry requirements. Thus, odd $J$ transitions are not possible. The upper state has both even and odd levels but is missing the zero rotational state. The absence of the zero rotational state occurs because the $v_1+v_2$ vibrational level has intrinsic angular momentum of $J=1$ and therefore the total angular momentum, $J$, cannot be less than one.

For molecules like CO, well approximated by the rigid rotor model, the relative line strengths can be accurately calculated and are most strongly dependent on the thermal distribution of the ground state populations. For CO$_2$ there are large departures from the rigid rotor model because of Coriolis interactions between the vibrational and rotational motions of the molecule. These effects have been studied and parametrised by what are called Herman-Wallis coefficients (Rothman et al., 1992b). Since we will rely on the relative strengths of lines within the $Q$-branch for some fits, these coefficients were assumed to be correct. The correction is largest for higher rotational states where the Coriolis interaction is strongest.

2.2 LINE SHAPE THEORY

In this chapter we discuss line shape effects with regard only to the molecule's internal motion. Translational effects are neglected until later and will be introduced as required. Here we introduce the simplest representation of line mixing effects, a band model of interacting lines where
the band shape is determined by the relaxation matrix. Through mathematical manipulation we will show how this band model of interacting lines can be represented on a line by line basis. There exist both first and second order expansions of the line by line representation which are discussed next. Finally we discuss methods of estimating the relaxation matrix.

Before discussing specific line shape effects we will outline a few general principles and definitions. To be consistent with the literature “ω” is used to represent frequency in radians per second although an equation written in terms of ω is often also valid for other frequency units. When experimental quantities are involved “ν” is used, in units of cm⁻¹. If there is still ambiguity, the units will be referred to explicitly.

Infrared absorption spectra are measurements of transmission through a cell filled with the gas of interest. Beer’s law, which relates the fraction of light transmission through the cell, \( \tau(\nu) \), to the absorption coefficient, \( k(\nu) \) in 1/cm, can be written,

\[
\tau(\nu) = e^{-Lk(\nu)},
\]

where \( L \) is the length, in cm, of the gas sample. The normalised line shape, \( I(\nu) \), is related to the absorption coefficient for a particular line, \( i \), by,

\[
k_i(\nu) = NS_iI(\nu)
\]

where \( S_i \) is the integrated strength of the absorption line in cm⁻¹/(molecules-cm⁻²) and \( N \) is the active gas density in molecules/cm³. When we refer to “line shape” we mean either the normalised line shape, \( I(\nu) \), or the absorption coefficient, \( k(\nu) \).

In all the theory discussed we will implicitly assume the binary collision, impact approximation. The binary impact approximation assumes that the duration of a collision is very small compared to the mean time between collisions and that collisions involve only two molecules at one time. In making this assumption we ignore the exact nature of the collision and are only interested in the changes in phase and velocity of the molecule before and after the collision. This is a standard assumption when discussing line shapes close to line centre, since the impact approximation is considered valid over a frequency range less than the reciprocal of the duration of collision, \( \nu^{-1} \). For CO₂ \( \nu \) is approximately 1ps which corresponds to 5cm⁻¹ (Hartman and Boulet, 1991). Since our experimental spectra are just over 1cm⁻¹ wide and lines further than 5cm⁻¹ from the centre of the
spectrum were ignored, the impact approximation should be valid.

It is in many cases easier, or more insightful, to work with line shapes in the time domain rather than in the frequency domain (Van Vleck and Huber, 1977). Although this can be achieved with a simple Fourier transform, it is only through the Wiener-Khintchine theorem that one gains physical insight into the time domain representation. The Wiener-Khintchine theorem relates the power spectrum of a temporal function to the Fourier transform of its autocorrelation function

$$ I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \chi(t) e^{i\omega t} dt \quad (2.4) $$

The autocorrelation function in the time domain relates how a function, \( \mu \), at time \( t' \) is correlated with itself at a later time \( t' + t \). It is defined by

$$ \chi(t) = \langle \bar{\mu}(t') \cdot \bar{\mu}(t'+t) \rangle \quad (2.5) $$

where \( \langle \cdot \rangle \) means an average over \( t' \), normalised such that \( \chi(0) = 1 \). This normalisation is necessary since a function is perfectly correlated with itself at zero time. It can also be shown that this normalisation leads to a normalised power spectrum. If one considers a radiating dipole, then the power spectrum of the radiation, \( I(\omega) \), is in fact the line shape and the autocorrelation function, \( \chi(t) \), expresses the correlation between the dipole, \( \bar{\mu} \), at time zero and itself at some later time, \( t \). An infinitely narrow line corresponds to an autocorrelation function which does not decay in time. However, translation and collisions perturb the molecule causing the autocorrelation function to decay with time. The fundamental properties of Fourier transforms mean that the faster the autocorrelation decay, the broader the line.

Since collisions decrease the coherence time of an absorbing molecule, the resulting collisional broadening scales with pressure and is called pressure broadening. Within the impact approximation and ignoring speed-dependence, it is often shown that the autocorrelation function for the pressure broadened line shape is just an exponential decay, \( e^{-2\gamma t} \). The power spectrum of this function is the standard Lorentzian line shape for an isolated, collision-broadened line, with a half-width at half maximum given by \( \gamma \). Shown below is the normalised Lorentz line shape, where \( v_0 \) is the line centre.
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\[ I(v)_{\text{Lorentz}} = \frac{1}{\pi} \frac{\gamma}{(v-v_o)^2 + \gamma^2}. \] (2.6)

The half-width, \( \gamma \), is related to the broadening coefficient, \( \gamma_0 \), by,

\[ \gamma = \gamma_0 P \]

where \( \gamma_0 \) is the half-width at 1 atmosphere and 296K and \( P \) is the pressure in atmospheres. As often done by the atmospheric community, we have used pressure instead of density throughout this work. This is a good approximation over the pressures studied here since the ideal gas law directly relates the two quantities. The half-widths are often empirically corrected for temperature using,

\[ \gamma(T) = \gamma(T_0) \left( \frac{T_0}{T} \right)^n \] (2.8)

where \( n \) is an empirically determined quantity (Bouanich, 1984; Nakazawa and Tanaka, 1982). This temperature correction is based on a simple kinetics argument which shows that the collision frequency increases linearly with density and mean molecular velocity. Since density varies as \( T^{-1} \) and molecular velocity varies as \( T^{0.5} \), the simple argument suggests \( n=0.5 \). Although this simple form has been found to be incorrect, it is still commonly used but with an empirically measured value for \( n \), which for CO\(_2\) lies between 0.64 and 0.78 (Rothman et al., 1992b).

2.2.1 LINE MIXING

The Lorentz line shape assumes that transition lines are isolated. Line mixing addresses the line shape, line shift, and line strength effects that occur when lines are not isolated. We introduce line mixing for the case of two lines as shown in figure 2.2. In the absence of any broadening mechanisms these two lines would be located at their precise resonant frequencies \( v_1 \) and \( v_2 \). However the effects of collisions broaden the two lines such that they overlap. This system is shown by an energy level diagram in figure 2.3 (Levy et al., 1992). The two initial states belong to the same vibrational level but have differing rotational levels and the same is true for the two final states. The transitions \( i_1 \rightarrow f_1 \) and \( i_2 \rightarrow f_2 \) represent the two resonant rovibrational transitions \( v_1 \) and \( v_2 \). Because the lines overlap, an absorbed photon of energy \( v \) can lead to either transition. This is represented in
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Figure 2.2. Two overlapping lines with resonant frequencies $v_1$ and $v_2$. Absorption at a frequency $v$ could be due to either line.

Figure 2.3. Simple two transition model of line mixing. Solid horizontal lines represent molecular energy levels, dashed horizontal lines represent perturbed energy levels. Dashed diagonal lines represent collisional coupling.
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Figure 2.3 by the transitions between perturbed energy levels $i_1 \rightarrow f'_1$ and $i_2 \rightarrow f'_2$, where the levels are perturbed as a direct result of the collisions that broaden the lines. Since the perturbed levels are temporary, they in fact represent the same molecular state as the unperturbed levels.

If we assume, as is often the case, the energy difference between the initial levels $i_1$ and $i_2$ is small relative to the kinetic energy of the molecules, then collisions will readily transfer the molecule between these two rotational energy states. The same applies to the two final states $f_1$ and $f_2$. Because the energy difference between vibrational states is generally larger, it is much less likely that kinetic collisions will cause a vibrational energy change. The picture thus consists of two vibrational levels, each with rotational levels coupled by kinetic collisions, i.e. rotationally inelastic collisions.

Rotationally inelastic collisions result in a coupling of the two transitions, $v_1$ and $v_2$. The coupling occurs because each transition $i \rightarrow f$ occurs via two possible paths. If we consider a photon of energy $v$ there are two paths for the transition $i_1 \rightarrow f_1$. One path is just the direct optical transition $(i_1;i_1') \rightarrow (f_1';f_1)$. The second path involves the molecule moving through states: $i_1 \rightarrow (i_2;i_2') \rightarrow (f_2';f_2) \rightarrow f_1$, where $\rightarrow$ indicates the transfer between states caused by collisions and $\rightarrow \rightarrow$ indicates an optical transition. If the complex probability amplitudes of the two paths are represented by $P_1$ and $P'_1$, the transition amplitude is given by $|P_1 + P'_1|^2$. Since both $P_1$ and $P'_1$ are complex quantities, this is not equal to $P_1^2 + P'_1^2$ which would correspond to isolated lines. The difference between the two quantities is referred to as interference effects. It is these interference effects that are called line mixing. The largest interference (line mixing) effects will be possible when $P_1$ and $P'_1$ are both relatively large. This will occur when the broadening is large enough that the lines overlap significantly and the two lines have appreciable absorption at the same frequency.

With this simple picture we can understand the two conditions necessary for line mixing to occur: 1) the energy difference between rotational levels must be sufficiently small such that thermal collisions can readily change the rotational state of the molecule; and 2) the lines must overlap significantly. The first condition is well met by the CO$_2$ molecule. At $T=296$K the mean kinetic energy, $k_B T$, is 206cm$^{-1}$ whereas the rotational constant is approximately $B=0.390$cm$^{-1}$ (Rothman et al., 1992b). Thus the rotational energy spacing is small compared to the molecule's translational energy, particularly for the lower $J$ states. This condition is also met by many other molecules at
atmospheric temperatures. The second line mixing condition will be satisfied when the transition frequencies \( v_1 \) and \( v_2 \) are closely spaced. Because the line shapes extend to \( v \pm \infty \), all lines overlap to some degree. But, the degree of line mixing is proportional to the amount of overlap and generally if the lines are separated by more than several half-widths, line mixing is negligible. This corresponds to the common statement: unless lines overlap appreciably they are isolated. We can also understand why line mixing does not occur between overlapping lines of different molecules since the coupled energy levels must be within the same molecule.

The two-transition model described above can be generalised to any number of transitions. The collisional processes which cause line mixing are then quantified by the relaxation matrix\(^5\), \( W \), where the off-diagonal elements, \( W_{jk} \) and \( W_{jp} \) represent the couplings of transitions \( |j\rangle \rangle \) and \( |k\rangle \rangle \).\(^6\) It will be shown that the real and imaginary parts of the diagonal elements equal the Lorentz broadening coefficients and the pressure-induced line shift coefficients respectively, \( W_{jj} = \gamma_j + i \delta_j \). Although all bands actually consist of an infinite number of transition lines, the band can be approximated by \( n \) strong lines with the weaker lines ignored. For a band consisting of \( n \) transition lines the relaxation matrix will be \( n \times n \) in size. There are actually less than \( n^2 \) independent elements since \( W_{jk} \) and \( W_{jp} \) are not independent quantities. Requiring the molecular system to be in thermodynamic equilibrium imposes a detailed balance condition on the relaxation matrix (Van Vleck and Huber, 1977) such that 

\[
\rho_j W_{jk} = \rho_k W_{kp}
\]

where \( \rho_k \) is the population of the lower energy level corresponding to transition \( k \).

Not all types of collisions couple transitions and hence not all collisions lead to line mixing. The coupling results only from rotationally inelastic collisions since the collisions must change the rotational state. Yet, other collisions can contribute to the line width without coupling the lines. An example of such collisions are vibrationally dephasing collisions which elastically dephase the molecule. We have taken the approach of explicitly separating the contributions to the line width from sources other than rotationally inelastic collisions, i.e. vibrational dephasing. We use \( W_{ij} \) to

\(^5\) We have used bold face to signify matrices, i.e. \( W \). Also note that our definition of the relaxation matrix is normalised to one atmosphere and the pressure is an explicit parameter. Some authors absorb the pressure into the relaxation matrix.

\(^6\) \( |j\rangle \rangle \) represents a transition line, i.e. an initial and final state pair \( |i, f\rangle \).
represent only the broadening resulting from rotationally inelastic collisions and \( \gamma_D \) to represent the broadening from all other collisions.

The first transmission profile to include line mixing was developed by Baranger (1958a; 1958b; 1958c; Fano, 1963). The form for the band transmission is,

\[
k(v) = \frac{N}{\pi} \text{Im} \left\{ \mu^\dagger \left[ (v-i\gamma_D)I-v_0-iPW \right]^{-1} \rho \mu \right\},
\]

where \( \mu \) is a column vector of the transition dipole moments; \( I \) is the identity matrix; \( v_0 \) is a diagonal matrix of transition frequencies; \( P \) is the total gas pressure in units of atmospheres; \( \rho \) is a diagonal matrix of lower state populations for each transition; \( \dagger \) means transpose and \( \text{Im} \) means the imaginary part.

Equation 2.9 represents the absorption coefficient for a band of interacting lines. There are three main limitations to this formalism: 1) the band shape does not include the translational effects of Doppler broadening or Dicke narrowing and it is difficult to see how to include these effects across the entire band; 2) the large matrix inversion required at each frequency makes it impractical to implement this equation in a radiance calculation; and 3) the equation offers little physical insight into the behaviour of the band. Diagonalising \( W \) and subsequent rearrangement of the band model equation will change it to a summation of lines. Using this approach we can address each of the shortcomings listed above.

Again following the review of Levy et al. (1992) we first represent equation (2.9) in component form,

\[
k(v) = \frac{N}{\pi} \text{Im} \left\{ \sum_{j,k} \mu_j \langle j|\left[ (vI-G-iPW)I^{-1}\right]|k\rangle \mu_k \rho_{kj} \right\},
\]

where we have defined \( G=v_0+iPW \). Next we assume that there exists a matrix \( A \), and a diagonal matrix \( \Lambda \) such that \( \Lambda=A^{-1}G\Lambda \), with elements \( \Lambda_{jj} \) being the eigenvalues of \( G \) and the column vectors \( \bar{A}_j \) being their respective eigenvectors, such that \( G\bar{A}_j=\Lambda_{jj}\bar{A}_j \). Since the matrix \( A \) also diagonalises the matrix \( [(v-i\gamma_D)I-G] \), we can calculate its inverse in terms of \( A \) and \( \Lambda \):
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\[
A^{-1}\left[ (v-i\gamma_D)I-G \right]A = (v-i\gamma_D)I - \Lambda
\]

\[
\left[ (v-i\gamma_D)I-G \right] = A\left[ (v-i\gamma_D)I - \Lambda \right]A^{-1}
\]

\[
\left[ (v-i\gamma_D)I-G \right]^{-1} = A\left[ (v-i\gamma_D)I - \Lambda \right]^{-1}A^{-1}.
\]

Because the matrix \([(v-i\gamma_D)I-\Lambda]\) is diagonal, its inverse is also diagonal with reciprocal diagonal elements. Since the matrix \(A\) is independent of \(v\), the calculation of \(A\), \(A^{-1}\), and \(\Lambda\) need only be done once at a given \(P\) and then equation 2.10 can be calculated quickly at any frequency. We continue by expanding the inverse in component form,

\[
\langle \langle j | (v-i\gamma_D)I-G \rangle^{-1} | k \rangle = \sum_m A_{jm} \left[ (v-i\gamma_D-\Lambda_m) \right]^{-1} A^{-1}_{mk},
\]

and substituting equation 2.12 into 2.10. The result is expressed as,

\[
k(v) = \frac{N \text{Im}}{\pi} \sum_{j,k,m} \left( \frac{\mu_j A_{jm} (A_{mk}^\dagger \mu_k \Phi)}{v-i\gamma_D-\Lambda_m} \right).
\]

Because the matrix \(G\) is non-Hermitian, its eigenvalues, \(\Lambda_m\), and eigenvectors, \(\Lambda_j\), will be complex. Since only the imaginary part of equation 2.13 contributes to the line shape, we will take the imaginary component by multiplying both the numerator and the denominator by the complex conjugate of the denominator \((v-i\gamma_D-\Lambda_m)^\dagger\). After some rearrangement the equation can be put in a form with more familiar terms:

\[
k(v) = \frac{N \text{Re} \Omega_{\mu} \text{Im} \left[ \Lambda_j + P\gamma_D \right]}{(\text{Re} \left[ \Lambda_j \right])^2 + (\text{Im} \left[ \Lambda_j \right] + P\gamma_D)^2} + \frac{\text{Im} \left[ \Omega_{\mu} \right] \left( v - \text{Re} \left[ \Lambda_j \right] \right)}{(\text{Re} \left[ \Lambda_j \right])^2 + (\text{Im} \left[ \Lambda_j \right] + P\gamma_D)^2}
\]

\[
\Omega = A^{-1} \mu \mu^\dagger A.
\]

This equation represents the absorption coefficient of a band as a sum of individual components. It represents the same line shape as equation 2.10 without any approximations. Each component includes two terms: the first term is symmetric and has a Lorentzian line shape while the second term is asymmetric and has a dispersion line shape. At very low pressures, matrix \(G\) is essentially diagonal with transition frequencies as diagonal elements. In this limit, the eigenvalues are simply the original frequencies, \(\Lambda_j = v_i\). Hence, we associate each component of equation 2.14 with a spectral line and re-write the equation to reflect its similarity with known line shape components.
The $v_i$ are line centres for the individual lines and the $\gamma_i$ are the half-widths of the Lorentzian lines. For the dispersion line shapes the $\gamma_i$ represent a measure of the dispersion width, which is the frequency separation between line centre and the maximum/minimum points of the dispersion line shape. The integrated strengths of the Lorentzian components are given by $p_i$, which at low pressure equals the usual isolated line strengths, $S_i=(p_i)_{\text{low pressure}}$. The $q_i$ cannot be related to the integrated strengths of the dispersion components because the integrated area under a dispersion line shape is zero. For this reason it may be more useful to think of $p_i$ and $q_i$ in a different way. When scaled by $N/\pi$, $p_i/\gamma_i$ is the maximum height of the Lorentz line shape and similarly, $q_i/\gamma_i$, is the maximum height of the dispersion component. Figure 2.4 shows the Lorentz and dispersion line shapes labelled with $p_i$, $q_i$, $\gamma_i$, and $v_i$.

Equation 2.15 is the fundamental equation which we will refer to many times in this thesis. Below we will discuss approximations of this general form and later we will add translational effects, however, equation 2.15 represents the full line mixing effects, without approximation, on a line by line basis.
2.2.2 LINE MIXING PERTURBATION EXPANSIONS

Before continuing with a general discussion of equation 2.15 it is worthwhile introducing two well known perturbation expansions. Rosenkranz (1975) performed a first order expansion, in pressure, of the matrices $A$ and $A^{-1}$. Although Rosenkranz assumed that the off-diagonal elements of the relaxation matrix were purely real, Lavorel et al. (1990a) generalised the expansion to include complex off-diagonal elements in the first order perturbation. The resulting first order line shape is as follows:

---

Figure 2.4. a) Lorentz and b) dispersion line shapes.
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\[ k(\nu) = \frac{N}{\pi} \sum_i S_i \left( \frac{P\gamma_0'(1-PZ_0')}{(\nu - \nu_0' - P\delta_o')^2 + (P\gamma_0')^2} + \frac{PY_0'(\nu - \nu_0' - P\delta_o')}{(\nu - \nu_0' - P\delta_o')^2 + (P\gamma_0')^2} \right) \]

where

\[ \gamma_0' = \text{Re}[W_{ii}] + \gamma_D, \quad \delta_0' = \text{Im}[W_{ii}], \quad Y_0' + iZ_0' = 2 \sum_{j=i} \frac{\mu_j}{\mu_i} \frac{W_{ij}}{\nu_i - \nu_j}, \quad \text{and} \quad S_i = \rho_i \mu_i^2; \]

and \( \gamma_D \) is as previously defined, \( \nu_0' \) are the isolated line frequencies, \( (P\gamma_0') \) are the Lorentzian half-widths, and \( (P\delta_o') \) are the linear pressure shifts, of line \( i \), in the low pressure limit. Note that the \( \gamma_0' \) and \( \delta_0' \) are just the real and imaginary parts of the relaxation matrix diagonal elements which, as stated earlier, are the low pressure broadening coefficients and linear pressure shift coefficients. The \( Y_0' \) and \( Z_0' \) are respectively the real and imaginary first order mixing coefficients in units of atm\(^{-1}\). The imaginary part of the mixing coefficient is usually zero since most authors assume the off-diagonal relaxation matrix elements to be purely real. Although this may not be true, the effects of the imaginary off-diagonal elements have been found to largely cancel each other (Boissoles et al., 1989).

Under the assumption of real off-diagonal elements, the \( Y_0' \) are known as the Rosenkranz first order mixing coefficients and equation 2.16 is the Rosenkranz profile. The new parameters, \( Y_0' \), are constants which state that the ratio of the peak dispersion height to Lorentz height, \( q/p_h \), increases linearly with pressure. Hence, the first order line mixing effect is to add a dispersion line shape which scales linearly with pressure to the isolated Lorentz line shape. The Rosenkranz profile is valid when the lines are weakly overlapped.

The expression for the Rosenkranz mixing coefficients gives some insight into the role of the off-diagonal elements. Equation 2.16 expresses the mixing coefficient, \( Y_0' \), as a sum of the couplings, \( W_{ii} \), between line \( |i\rangle \) and every other line. Both the off-diagonal relaxation matrix elements and the frequency separation of the two lines determine the extent of coupling. The larger the off-diagonal elements the greater the degree of line mixing. Because the frequency separation term occurs in the denominator, very closely spaced lines can experience a large degree of line mixing.

Equation 2.16 leads one to think that only \( W_{ii} \) represents the coupling of line \( |i\rangle \) to \( |j\rangle \), which does not match the simple picture earlier described where both rates \( W_{ii} \) and \( W_{ij} \) impact on the line mixing of line \( |i\rangle \). In fact the Rosenkranz expression hides the true symmetry which was derived.
using detailed balance from the mixing coefficients expressed as,

\[
y^i_o = \frac{1}{S_i} \sum_{j \neq i} \mu_i \mu_j \frac{W^i_j \rho_i + W^j_i \rho_j}{v_i - v_j},
\]

which better agrees with the physical interpretation of line mixing previously described.

Smith (1981) also performed a perturbation expansion of equation 2.15, keeping terms to second order in pressure. To first order this expansion agrees with Rosenkranz's, but Smith's second order effects include a quadratic pressure shift and a quadratic strength term. Equation 17 of Smith's paper can be written as follows:

\[
k(v) = \frac{N}{\pi} \sum_k S_k \frac{P Y^k_o (1 + P^2 g_k) + P Y^k_o (v - v_o - P \delta^k_o - P^2 \Delta_k)}{(v - v_o - P \delta^k_o - P^2 \Delta_k)^2 + (P Y^k_o)^2},
\]

where the quadratic pressure shift coefficient is given by,

\[
\Delta_k = \sum_{j \neq k} \frac{W^j_k W^j_k}{v^j_k},
\]

and the quadratic strength coefficient is given by,

\[
g_k = \sum_{j \neq k} \frac{W^j_k W^j_k}{v^j_k} - \left[ \sum_{j \neq k} \frac{(\mu_j / \mu_k) W^j_k / v^j_k} \right]^2 + 2 \sum_{j \neq k} \frac{(\mu_j / \mu_k) W^j_k W^j_k / v^j_k} - 2 \sum_{j \neq k} \sum_{l \neq k} \frac{(\mu_j / \mu_k) W^l_k W^l_k / v^l_k v^l_k}{v^l_k v^l_k}.
\]

The definition of \(Y^k_o\) remains the same as in the Rosenkranz equation 2.16. The above expansion assumes that the off-diagonal elements of the relaxation matrix are real although Thibault et al. (1992a) has derived this equation with complex off-diagonal elements.

Smith's expansion adds two new features to the line shape. The line frequency now has a quadratic pressure dependence with coefficient \(\Delta_k\) defined by equation 2.19. The symmetric strength component also has a quadratic pressure dependence given by \(g_k\) and defined by equation 2.20.

---

\(^7\) Several typographic errors occur in Smith (1981) which have been corrected above. In equation 2.18 or Smith's equation 17 the term "\(+P^2 \Delta_k\)" appears instead of "\(-P^2 \Delta_k\)" and in equation 2.20 or Smith's equation 16 the summation over \(t\) had been omitted.
In summary, a band of lines can be represented as a sum of individual lines each with an associated dispersion component as given by equation 2.15 regardless of the pressure. This line shape is always valid; only the values of the parameters change with pressure. Table 2.1 lists four pressure regimes and the equations of the four relevant line shape parameters. At sufficiently low pressures the line mixing effects are negligible and the lines can be assumed isolated. As the pressure increases it is necessary to use the Rosenkranz line shape where the dispersion component, linear in density, becomes important. At yet higher pressures the Smith line shape includes a quadratic pressure dependence of the strength and frequency. In pressure regions where the line mixing effects are very strong we must take into account higher order density terms. This requires the full relaxation matrix. But we stress again, that regardless of the density, the line mixing effects can be represented on a line by line basis with the inclusion of a dispersion line shape associated with each Lorentzian component.

<table>
<thead>
<tr>
<th>Pressure Parameter</th>
<th>Isolated Line</th>
<th>Weak Overlap Rosenkranz</th>
<th>More Overlap Smith</th>
<th>Strong Line Mixing Baranger</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p_i )</td>
<td>( S_i )</td>
<td>( S_i )</td>
<td>( S_i(1+P^2 \gamma) )</td>
<td>( \text{Re}[\Omega_{\mu}] )</td>
</tr>
<tr>
<td>( q_i )</td>
<td>0</td>
<td>( P \gamma S_i )</td>
<td>( P \gamma S_i )</td>
<td>( \text{Im}[\Omega_{\mu}] )</td>
</tr>
<tr>
<td>( \gamma_i )</td>
<td>( P \gamma S_i )</td>
<td>( P \gamma S_i )</td>
<td>( P \gamma S_i )</td>
<td>( \text{Im}[\Omega])</td>
</tr>
<tr>
<td>( v_i )</td>
<td>( v_i + P \delta S_i )</td>
<td>( v_i + P \delta S_i )</td>
<td>( v_i + P \delta S_i + P^2 \Delta_i )</td>
<td>( \text{Re}[\Omega])</td>
</tr>
</tbody>
</table>

2.3 RELAXATION MATRIX ESTIMATES

The main obstacle to the inclusion of line mixing in line shape calculations is a lack of knowledge about the relaxation matrix itself. The diagonal elements, being just the Lorentz line widths and linear pressure shift coefficients, can ideally be measured at low pressures where the lines of the band are well isolated, but the off-diagonal elements generally defy such measurements. Direct
measurement of the off-diagonal elements has been achieved only in a few special circumstances where the majority of the matrix elements are assumed to be zero (Sinclair et al., 1993). Pump probe techniques have been used to measure state-to-state collision rates in some molecules such as HF (Hinchen and Hobbs, 1976; Copeland and Crim, 1983) but such experiments have yet to determine the necessary state to state rate in CO₂. Instead, one customarily estimates the off-diagonal elements using a set of rules and approximations (DePristo, 1978; Brunner and Pritchard, 1982; Steinfeld et al., 1991). Below we will outline the typical approach to this problem as outlined by Levy et al. (1992).

We start by introducing the inelastic collision rate, \( \kappa_{jk} \), which represents the probability rate of a collision taking a molecule from rotational state \( k \) to \( j \). As a first approximation, assume that the collision rate is independent of vibrational level. It has been shown that for isotropic Raman spectra (Levy et al., 1992) under the above approximation, the relaxation matrix elements are equal to the negative of the inelastic collision rates,

\[
W_{jk} = -\kappa_{jk} .
\]

Furthermore the relaxation matrix elements obey a sum rule: the sum of the relaxation elements from any column add to zero. Thus, the sum rule relates the collision rates to the line widths,

\[
W_{kk} = \gamma_k = -\sum_{j \neq k} \kappa_{jk} .
\]

Because the gas is in thermodynamic equilibrium, the rate of transfer from state \( k \) to \( j \) must be equal to the rate of transfer from \( j \) to \( k \). This is referred to as detailed balance and as with the relaxation matrix itself can be expressed as,

\[
\rho_k \kappa_{jk} = \rho_j \kappa_{kj} ,
\]

where \( \rho_k \) is the population of the state \( k \).

Equations 2.21, 2.22 and 2.23 alone cannot determine the relaxation matrix. The usual procedure is to introduce a parametrisated gap or scaling law to calculate the rates \( \kappa_{jk} \). These semi-empirical laws express the likelihood of collisional transitions as a function of the difference in energy levels. This corresponds to the physical picture shown in figure 2.5 where the magnitude of the off-
diagonal elements decay with distance from the diagonal. Hence, closely spaced lines interact more strongly than widely spaced lines.

A technique described by Strow and Gentry (1986) and Gentry and Strow (1987) to calculate the off-diagonal elements from measurements of the Lorentz line widths makes assumptions that can be best justified by their success in fitting spectra (Berman et al., 1997). Controversy arises because equations based on 2.21 and 2.22 are only strictly true for a tensor order \( q = 0 \) process (i.e., isotropic Raman spectra) and infrared spectra have tensor order \( q = 1 \). This issue is discussed by Green (1989; 1992) and Levy et al. (1992).

Strow and Gentry use an exponential power gap, EPG, law expressed as follows

\[
\kappa_{jk} = a \left( \frac{E^{jk}}{k_b T} \right)^{-b} \exp \left( \frac{-c \Delta E_{jk}}{k_b T} \right). \tag{2.24}
\]

The difference between the lower energy states of the transitions is given by \( \Delta E_{jk} \); \( k_b T \) has its usual meaning, and \( a, b, \) and \( c \) are parameters to be determined. With this gap law, the collision rate decays...
to zero as a power for low energy differences and an exponential at higher energies. The scaling law is used to calculate upward transition rates, \( j>k \), and then detailed balance is used to calculate the downward rates. The diagonal elements are related to the off-diagonal elements using a modified sum rule (Edwards and Strow, 1991)

\[
W_{jj}^{\text{even}} = \frac{1}{2} \left( \sum_{k_{\text{even}}<j} \kappa_{kj}^{\text{even-even}} \right) + \frac{1}{2} \left( \sum_{k_{\text{odd}}<j, \neq 0} \beta \kappa_{kj}^{\text{even-even}} + \sum_{k_{\text{odd}}>j} (1-\beta) \kappa_{kj}^{\text{odd-even}} \right) .
\] (2.25)

The sum law has been modified to account for the CO\(_2\) spectroscopy. Essentially, the sum law allows for the total collision rate out of a given level \( j \) to contribute to the line width. However, equation 2.24 assumes that the rates, \( \kappa \), are independent of vibrational level, which is probably not true for the \( v_1+v_2 \) band. The upper vibrational level has both even and odd rotational levels whereas the ground vibrational level has only even rotational levels. Because there are only even transitions for the \( v_1+v_2 \) band, \( j \) must be even. The modified sum rule above assumes that the total rate out of level \( j \) is approximately equal for the upper and lower vibrational states. In the ground state only even–even collisions are possible but in the upper states odd–even collisions are also possible. The \( \beta \) parameter allows for a division between even–even collisions and odd–even collisions in the upper vibrational level, with \( \beta=0.5 \) being no preference. The even–even rates from state \( j \) to \( k \) are given by \( \kappa_{jk}^{\text{even}} \) in the lower vibrational level and \( \beta \kappa_{jk}^{\text{even}} \) in the upper vibrational level.

The gap law parameters \( a, b, \) and \( c \) determine the off-diagonal rates which in turn determine the line widths. The gap law parameters are adjusted to optimise the agreement between the calculated line widths and the experimentally measured line widths.

Because the collision rates in the ground and upper vibrational levels are different, one cannot longer apply equation 2.21 to find the off-diagonal relaxation matrix elements. Instead, we assign the negative of the upper vibrational level collision rates

\[
W_{jk} = -\beta \kappa_{jk}^{\text{odd}} .
\] (2.26)

This is justified by the calculations performed by Green (1989) where it is shown to be a good approximation.
CHAPTER 3

BACKGROUND

Line mixing is of such current interest that a comprehensive list of the work that has been done in the last 20 years would contain several hundred references. The review by Levy et al. (1992) contains a large number of the references published before that date. These works discuss line mixing in the $P$, $Q$, and $R$-branches for a variety of molecules. Some are theoretical and others experimental. However, only a few of these papers describe direct measurements of line mixing. The vast majority of experimental papers describe experiments which test the accuracy of a relaxation matrix model by comparing, not fitting, calculated spectra with experimental spectra.

Among the first experimental investigations of line mixing in a CO$_2$ $Q$-branch spectra were made by Strow and Gentry (1986) and Gentry and Strow (1987) with the investigation of the $3v_2$ band at 1932cm$^{-1}$ and the $v_1$+$v_2$ band at 2077cm$^{-1}$ respectively. The spectra were taken using a tunable diode laser spectrometer (TDLS) instrument with a resolution of approximately 0.0002cm$^{-1}$. The line mixing effects were calculated from a relaxation matrix whose off-diagonal elements were estimated using the exponential power gap (EPG) law.

The 2077cm$^{-1}$ paper included spectra ranging in pressure from 13kPa (100Torr) to 96kPa (720Torr). Gentry and Strow did not fit for line mixing coefficients but compared the experimental spectra to theoretical spectra calculated using equation 2.9. The measured spectra showed large departures from a straightforward summation of Lorentzian line shapes but reasonable agreement with the line mixing spectra.

A major contribution of these works was their method to compensate for the missing odd energy levels in the lower energy state. These have since been referred to as “ad hoc” approximations by other authors, but also recognised as being reasonably accurate (Green, 1989; 1992).
Figure 3.1. Results from Gentry and Strow (1987). (a) Experimental and calculated transmission of the self-broadened $v_1+v_2$ Q-branch of CO$_2$. Pressure is 18.8kPa (143Torr). $\Delta$ = Lorentz calculation, + = line mixing theory, solid line = experimental spectrum. (b) Experimental and calculated absorption coefficients. Below these plots is the percent deviation of the Lorentz (-----) and line mixing (-----) calculations from the observed absorption coefficients.

Figure 3.1 shows their results for pure CO$_2$ at 18.8kPa (143Torr). It is difficult to assess the residual on the chosen scale but the difference between the observed spectrum and the calculated spectrum is on the order of 5% over the region of appreciable absorption. The contributions to the
residual were undetermined by the paper but could come from several sources: inaccurate off-
diagonal elements, inaccurate broadening coefficients, the exclusion of translational effects from the
model or other line shape inadequacies. In a later paper, Edwards and Strow (1991) acknowledged
that a key to the success of their relaxation matrix was that the final band shape was only weakly
dependent on the exact value of the relaxation matrix. The very existence of the residual, however,
is an indication that more information lies within the spectra. In this thesis we have placed much
greater emphasis on minimising the structure in the residual.

Strow and Pine (1988) presented a similar analysis of an N$_2$O $Q$-branch but with
measurements taken using a difference frequency system. They used equation 2.15 to generate spectra
and compare with measured spectra up to one atmosphere. The relaxation matrix was calculated
using a technique very similar to that of Gentry and Strow (1987) but included collision selection
rules between even and odd rotational levels. They were able to show that collision selection rules
led to much better agreement with the measured spectra. These methods were further developed over
the next few years, (Edwards and Strow, 1991; Strow et al., 1994).

Much of the other work on line mixing has centred around the application of gap laws to the
modelling of the relaxation matrix, most notably the energy corrected sudden (ECS) and modified
exponential gap (MEG) laws. In particular, a large body of both theoretical and experimental work
on CO$_2$ has been performed by groups in France (Boissoles et al., 1989; 1994a; 1994b; 1994c; 1996;
1997; Bonamy et al., 1993; 1997; Thibault et al., 1992a; 1992b, 1994). They use approximate
quantum methods such as the ECS and infinite order sudden (IOS) theories to calculate the relaxation
matrix. These models are extensions of the theoretical work done by Green (1989). These papers
have developed the ECS model for relaxation matrix calculations to the point where agreement
between calculated and measured spectra is very good. Again these are comparison studies as
opposed to fitting studies. The experimental spectra were taken using Fourier transform instruments
and the emphasis was usually on measurements made at greater than 0.5 atmospheres. Only the work
of Bonamy et al. (1993) has looked at this band or at pure CO$_2$, but no fitting for spectral parameters
was done. The measurements were made with a diode laser at pressures greater than 1 atmosphere.

Only two papers of other authors are known which discuss direct line mixing measurements
in the infrared, Thibault et al. (1992a) and Pine (1997b). Thibault et al. (1992a) made direct measurements of very weak line mixing effects in CO by relating the pressure shift of the intensity maximum to an apparent quadratic pressure shift induced by line mixing. This apparent shift is not the second order line mixing shift of Smith (1981) but rather an interpretation of first order mixing effects. This technique allowed them to measure first order mixing coefficients for many P- and R-branch lines at pressures below 8 atmospheres. This technique was possible for the P- and R-branches because the lines were well separated. It could not be applied to the branch we studied since the intensity maxima of the Q-branch lines were not clearly resolved at any but the lowest pressures.

Pine (1997b) has recently made direct line mixing measurements of R- and P-branches in CH$_4$ broadened by N$_2$ and Ar, using a difference frequency spectrometer. The R- and P-branch lines of CH$_4$ are degenerate and therefore each line is actually a multiplet of very closely spaced lines. In this paper Pine presents a similar analysis to that presented in this thesis and a previous publication (Berman et al., 1997). First order line mixing coefficients were measured within the Rosenkranz approximation for several multiplets of lines.

The papers discussed above are most closely related to the work of this thesis. Of these papers, only Pine (1997b) has made direct measurements of line mixing. By far the largest number of experimental studies act simply to verify the accuracy of a relaxation matrix estimation.
CHAPTER 4

EXPERIMENTAL

All the absorption profiles in this thesis were measured using a difference frequency spectrometer (Pine, 1974). The heart of the instrument is a LiIO₃ non-linear crystal which generates narrow band infrared radiation at the difference frequency of two single frequency visible lasers. Tuning the frequency of one of the input lasers, tunes the infrared output frequency. Through attention to detail, we achieved a signal-to-noise ratio in excess of 2000:1 and a frequency resolution of ±1.5MHz (5×10⁴cm⁻¹) over scan widths of 40GHz (1.3cm⁻¹).

The infrared (IR) apparatus has undergone an evolutionary process of improvement over the last ten years. The modifications that made the most significant improvement to the IR spectra were changes in the non-linear crystal configuration, the addition of Brewster windows to the gas cell and the detector chambers, the use of stainless steel tubing for gas transport, and changes to the data acquisition software.

First we discuss the experiment from a design and mechanical point of view. I have divided the experimental apparatus into four broad sections: (1) generation and detection of infrared radiation, (2) visible optics and frequency measurement, (3) signal processing and software, and (4) gas handling. In the final section (5) of this chapter we discuss the methodology of performing the experiment. Unless stated otherwise, the information in this chapter applies to the state of the instrument when the last experimental spectra were taken. However, when relevant, previous experimental configurations are described along with the reasons for the changes.
4.1 INFRARED GENERATION and DETECTION

4.1.1 Principles of Difference Frequency Generation

Overlapping two visible laser beams inside a LiIO₃ crystal can, under the right conditions, produce IR radiation at a frequency equal to the difference between the frequencies of the two input beams. This non-linear interaction, known as difference frequency generation, created the narrow band, tunable, infrared radiation source for the experiments. Here we outline some of the important concepts and properties as they pertain to this application. The reader is referred to other sources (Boyd, 1992; Boyd and Kleinman, 1968; Yariv, 1976; Pine, 1974; 1976) for more information on the general principles behind difference frequency generation and to the theses of Duggan (1995; 1990) for other details of our implementation.

Difference frequency generation is possible within many materials because the induced polarisation has a non-linear dependence on the applied field. This non-linearity creates polarisation components at harmonics of the applied field and at the sum and difference frequencies. The induced polarisation in turn radiates at these new frequencies. The induced polarisation inside the crystal, \( \vec{P} \), is related to the applied field, \( \vec{E} \), by the linear and non-linear susceptibilities of the crystal, \( \chi^{(1)} \), \( \chi^{(2)} \), ..., where, using the summation convention\(^8\):

\[
P_i = \varepsilon_0 \left( \chi^{(1)}_{ij} E_j + \chi^{(2)}_{ijk} E_j E_k + \ldots \right) .
\]

(4.1)

It is the quadratic terms that generate the difference frequency radiation and so we ignore higher order terms. Let us set aside, for a moment, the question of which polarisation components we use. The second order polarisation for a given component can then be expressed as,

\[
P^{(2)}(t, \vec{r}) = 2 \varepsilon_0 d_{\text{eff}} \left( E_{\omega_1}(t, \vec{r}) \cdot E_{\omega_2}(t, \vec{r}) \right) .
\]

(4.2)

The effective non-linear coefficient, \( d_{\text{eff}} \), has replaced the susceptibility tensor.

Assuming the fields to be plane waves with wave vector, \( k \), in the \( \hat{z} \) direction, they can be

\(^{8}\) The superscript \( (n) \) represents the \( n^{th} \) order. The subscripts \( i, j, \) and \( k \) each represent one not necessarily unique orthogonal axis. The summation convention sums over repeated indices, e.g. \( b_{ij} c_{jk} = \sum_j b_{ij} c_{jk} . \)
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represented as follows,

\[ E_{\omega_1}(t,z) = \frac{E_{\omega_1}}{2} \left( e^{i(\omega_1 t - k_1 z)} + e^{-i(\omega_1 t - k_1 z)} \right). \] (4.3)

For input fields \( \omega_1 \) and \( \omega_2 \), the time dependence of the induced polarisation at a particular location \( z=0 \) is found by substituting equation 4.3 into equation 4.2:

\[ P^{(2)}(t,z=0) = \varepsilon_0 d_{\text{eff}} \left[ E_{\omega_1} E_{\omega_2} e^{i(\omega_1 + \omega_2)t} + E_{\omega_1} E_{\omega_2} e^{i(\omega_1 - \omega_2)t} \right] + \text{c.c.}, \] (4.4)

where c.c. means complex conjugate. Thus, the induced polarisation has frequency components at the sum and difference frequencies of the applied fields. The second term in the square bracket is the difference frequency term, \( \omega_3 = \omega_1 - \omega_2 \).

This equation represents only the time dependence of the induced polarisation at point \( z_0 \). The total generated field will be determined by the integrated effect of the induced polarisation along \( z \). Therefore, appreciable power will be generated only if the induced polarisation along \( z \) constructively interferes. Re-deriving equation 4.4 with spatial dependence we find that the necessary phase matching condition is \( k_3 = k_1 - k_2 \) (Boyd, 1992). The conditions for infrared generation can therefore be summarised by the following two equations:

\[ \omega_3 = \omega_1 - \omega_2 \]
\[ n_3 \omega_3 = n_1 \omega_1 - n_2 \omega_2. \] (4.5)

If the medium is non-dispersive \((i.e.\) the refractive indices are frequency independent) then \( n_1 = n_2 = n_3 = \text{constant} \) satisfies both conditions simultaneously. But if the medium is even slightly dispersive then \( n_1 \) and \( n_2 \) must differ in such a way as to satisfy equation 4.5; this is the phase matching condition.

Angle tuning is a common technique for satisfying the phase matching criteria which uses the birefringence of certain non-linear crystals to advantage. This is most easily explained for uniaxial crystals which are birefringent crystals with a unique optic axis. The index of refraction in such crystals is a function of the wave vector orientation and polarisation. Light with polarisation perpendicular to the plane formed by the wave vector and optic axis is said to be of ordinary polarisation with index of refraction \( n_o \). Light that is polarised in the plane formed by the wave vector...
and optic axis is said to be extraordinary and the index of refraction is given as a function of the angle \( \theta \), between the optic axis and the wave vector \( k \),

\[
\frac{1}{n_e^2} = \frac{\cos^2 \theta}{n_o^2} + \frac{\sin^2 \theta}{n_o^2}
\]

where \( n_e \) is the index of refraction for light with extraordinary polarisation and \( \theta = 90° \). Hence, by using applied fields \( E_1 \) and \( E_2 \) with extraordinary and ordinary polarisations respectively, the crystal angle (i.e. \( \theta \)) can be adjusted to tune the extraordinary refractive index such that the phase matching criterion is matched.

We originally chose to use a LiIO\(_3\) crystal because it had the necessary characteristics to study the 4.7\( \mu \)m CO band. The characteristics considered in selecting LiIO\(_3\) were its near transparency, large non-linear susceptibility, and uniaxial birefringence. LiIO\(_3\) is transparent to visible wavelengths through to infrared wavelengths up to 6\( \mu \)m. It also has a relatively large non-linear susceptibility which allows for a high conversion efficiency. We found it performed well over a broad region extending from 2.2\( \mu \)m to 5.5\( \mu \)m.

The geometry of the crystal, the crystal axes and the incoming polarisations we used are shown in figure 4.1. The argon laser, \( E_{\text{Ar}} \), has extraordinary polarisation and the dye laser, \( E_{\text{dye}} \), has ordinary polarisation. The infrared output beam also has ordinary polarisation. This is known as type I phase matching, since the two lower frequencies have the same polarisations.

By adjusting the angle of the crystal, \( \theta \), we tuned the refractive index such that \( n_e \) satisfied equation 4.5. The crystal was cut with the optic axis at 22° to the normal of the front face which is the phase matching angle for 4.4\( \mu \)m (2273\( \text{cm}^{-1} \)) generation. At this frequency the incidence angle for the incoming beams was nearly normal.
Figure 4.1. Schematic of the crystal axes and beam polarisation orientation. Both the optic axis and the wave vectors lie in the plane of the page. The double refraction angle is $\alpha$ and the angle between the optic axis and the wave vectors is $\theta$.

Also shown in the figure is the double refraction of the Ar$^+$ beam. Because the crystal is birefringent and the electric field of the Ar$^+$ beam is not orthogonal to the optic axis, the Ar$^+$ beam experiences double refraction, which means that the direction of energy propagation is not parallel to the wave vector. For our geometry the double refraction angle, $\alpha$, was approximately $3^\circ$ and therefore the Ar$^+$ and dye laser beams did not propagate collinearly within the crystal, but overlapped only within a limited interaction region. Since the polarisations of the generated infrared radiation and the dye beam were perpendicular to the optic axis, these two beams did not experience double refraction. Thus, the beams cross and the region of interaction is limited by the finite beam widths.

Until now we have only discussed phase matching in terms of plane waves which are mathematically simple, but physically unrealisable. A more complete development would use Gaussian beams instead of plane waves. Including Gaussian beams adds complication but does not change the nature of the results (Yariv, 1976). In the next paragraphs we consider the generated IR power and
it becomes necessary to consider beams of finite width. For simplicity we will assume a hard-edged beam with a rectangular cross section. This turns out to be a reasonable approximation for a well-collimated Gaussian beam, with the primary difference being a constant of proportionality.

Two visible pump beams only generate infrared radiation where they overlap within the crystal. The size of the interaction region shown in figure 4.2 largely determines the intensity of the generated IR radiation. For a more rigorous calculation of the generated power, assuming Gaussian beams, see Harper and Wherrett (1977) or Boyd and Kleinman (1968). We now develop an equation of proportionality between the generated IR power and several factors involved in its generation. This development is based on simple physical principles but captures the essential concepts. The length of the interaction region is given by \( L = h_{\text{Ar}} \tan \alpha \) to a maximum of the crystal length, where \( h_{\text{Ar}} \) is the vertical beam width. The vertical extent of the interaction region is given by the vertical width of the dye beam, \( h_{\text{dye}} \), and the horizontal extent of the interaction is defined by the smaller of the dye and Ar\(^+\) beam widths, \( \min(\text{w}_{\text{dye}}, \text{w}_{\text{Ar}}) \). The cross sectional area is then \( hw \).

With the definitions above, we can create an equation of proportionality between the power of generated infrared radiation and several factors related to its generation. Equation 4.4 shows that the generated field is proportional to the product of the two input fields. Each phase matched interval in the direction of propagation adds to the infrared field already generated. In the weak field limit the generated field builds linearly with length, \( E_{\text{IR}} \propto E_{\text{Ar}} E_{\text{dye}} L \). Since the intensity is proportional to the square of the field and the power, \( P \), is equal to the intensity, \( E_{\text{IR}}^2 \), times the cross sectional area,
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$A_{interaction}$ the power can be expressed as:

$$P_{IR} \propto E_{IR}^2 A_{interaction}.$$  \hspace{1cm} (4.7)

With the appropriate substitutions we find,

$$P_{IR} \propto \left( \frac{P_{Ar}}{A_{Ar}} \right) \left( \frac{P_{dye}}{A_{dye}} \right) L^2 A_{interaction} = P_{Ar} P_{dye} \frac{h_{Ar} \min(w_{Ar},w_{dye})}{w_{Ar} w_{dye} \tan^2 \alpha}. \hspace{1cm} (4.8)$$

This first expression shows that the infrared power is proportional to the power density of the incoming beams, the square of the interaction length, and the cross sectional overlap area. Thus, a principal design criterion for maximum power is the maximisation of the interaction length which, if not for the double refraction phenomenon, would be a trivial problem. The second expression shows how the power varies in terms of the actual beam shapes (vertical and horizontal widths) and the double refraction angle, $\alpha$.

The simplest beam geometry would have two circular beams of equal size. The power in equation 4.8 is then independent of the beam sizes to a maximum determined by the crystal length, $h < l \tan \alpha$ where $l$ is the crystal length. This geometry is not, however, the optimum geometry for power. Two methods we employed to increase the infrared power are discussed in the next section.

4.1.2 LiIO₃ Crystal Configurations and Beam Geometries

There were two primary considerations in selecting a crystal configuration: IR output power and IR beam quality. Since a Gaussian beam was easiest to control and to focus onto the detectors, I sought to achieve an IR beam shape as close to Gaussian as possible. Other issues were simplicity and ease of operation.

Originally, the system used a single 1cm LiIO₃ crystal with circular beams of equal size. However starting in 1992 we endeavoured to improve the system by using alternative beam and crystal geometries.

---

We have implicitly assumed that the crystal is 100% transparent but in fact the LiIO₃ crystal has appreciable absorption in the infrared. For longer length crystals this would be an issue.
An interesting method of increasing the interaction length uses a pair of crystals with the second crystal reversed. Figure 4.3 illustrates the two crystal geometry. Reversing the second crystal inverted the optic axis such that double refraction causes the Ar\(^+\) beam to cross the dye beam twice. With the interaction length doubled, the generated infrared power theoretically increases by a factor of four, according to equation 4.8. Using two uncoated 4mm crystals we witnessed an increase in power by a factor of three over a single crystal. The crystal surfaces were left uncoated because of the difficulty in finding anti-reflection coatings for the inner faces over the wide range of visible and infrared frequencies required. The first and last faces need only be anti-reflection coated for visible and infrared frequencies respectively. The absolute power was determined by Duggan (1995) to be about 10 nW.

Although this technique did effectively increase the output power, it had a few disadvantages. The number of crystal surfaces created multiple reflection paths which led to interference problems. Because many of these multiply reflected beams overlapped within the crystal, interference between these beams affected the infrared power. The power fluctuated by as much as 50% over a 1cm\(^{-1}\) scan,
with a frequency period that corresponded to the 4mm long LiIO$_3$ crystals of refractive index $n=1.8$. Ideally these fluctuations should have normalised completely$^{10}$ but in practice they did not. In addition, it was difficult to focus all the multiply reflected beams onto the detectors, and therefore a fraction of the infrared power was unmeasured. Interference effects changed the spatial distribution of energy in the infrared beam as function of frequency which changed the power striking the detectors and in turn changed the normalisation ratio. It was possible to reduce these effects with careful alignment but it was tedious and time consuming. It was necessary to phase match both crystals each time the frequency was changed and invariably this would lead to the normalisation problems discussed above. Despite the difficulties mentioned above, the two crystal configuration produced excellent results when carefully aligned (Duggan et al., 1995).

As an alternative to the two crystal configuration we returned to the single 1cm crystal but with a tailored beam geometry (Bawendi, 1988; Volkov, 1981). The crystal was broadband anti-reflection coated for visible light on the input face and broadband anti-reflection coated for the infrared on the output face. Maximising the power as given by the right side of equation 4.8 requires that the beam geometry maximises the Ar$^+$ vertical width and minimises the horizontal widths of both the Ar$^+$ and dye beams. Essentially the increase in the vertical width of the Ar$^+$ beam trades off a decrease in power density for an increase in the interaction length. Because the power increases with the square of the interaction length there is a net gain.

The size of the Ar$^+$ beam in the vertical axis was adjusted using a cylindrical lens. The cylindrical lens was oriented such that the horizontal width was unchanged. With this lens we increased the Ar$^+$ vertical width and therefore increased the interaction length to the limit imposed by the length of the crystal. The upper limit is $h_{Ar}=ltan\alpha$, which for $l=1$cm and $\alpha=3^\circ$ was $h_{Ar}=520\mu$m.

The practical limit of how narrow the vertical and horizontal widths should be made was not as definite. The properties of Gaussian beams make the use of very small beam waists impractical. The confocal parameter, $z_o$, is the propagation distance over which a Gaussian beam diameter increases by a factor of $\sqrt{2}$. It is related to the beam waist radius, $w_o$, by $z_o=\pi w_o^2/\lambda$ (Siegman, 1986). Therefore the smaller the diameter of the beam waist the more rapidly the diameter increases away

$^{10}$Normalisation of the infrared power is described later in section 4.3.
from the beam waist. Duggan (1990) suggested that the confocal parameter could be as short as 0.02cm, corresponding to a beam diameter of only 6μm, but such small diameters would be difficult to control and maintaining overlap would require sensitive feedback controls. If we consider the two visible beams to have beam waist diameters of 100μm, the confocal parameters would be approximately 1.5cm. Because the infrared beam is the product of the two visible beams its waist is reduced to 100/√2μm, and the much longer wavelength results in a corresponding confocal parameter of only 1.5mm. At distances far from the beam waist the beam diverges at a constant angle referred to as the divergence angle. In the case described above the divergence angle for the infrared beam is 2.7° and the beam diameter is approximately 5mm in size only 10cm from the beam waist. Note, however, that if the visible beam waists were reduced to 50μm then the infrared beam diameter, 10cm from its waist, would be over 2cm and too large to pass through the cell. For this reason we kept the visible beam waists greater than 75μm.

The system we used set the vertical and horizontal widths of the Ar+ and dye beams at approximately 540μm×110μm and 110μm×110μm at their respective waists. Although I would have preferred to make the horizontal widths narrower, the optics available made such a highly astigmatic beam difficult to achieve. Substituting the numbers for this geometry into equation 4.8 suggests a five-fold improvement over non-astigmatic beams. Although a direct power comparison with the non-elliptical single crystal geometry was never performed, we estimated a factor of 3.5 to 4 increase in power. Note that the generated infrared beam was only mildly astigmatic with a vertical-to-horizontal ratio of √2:1.

This geometry was easier to use and performed better than the previous double crystal configuration. Because the Ar+ beam height was large, 0.5mm, the problem of initially overlapping the beams essentially reduced to a one-dimensional problem. Because of the anti-reflection coatings and only one pair of parallel crystal surfaces, the problems caused by multiple reflections were drastically reduced. This reduced the power variation over a 1.3cm scan to less than 10%, usually. The fact that there was only one crystal resulted in a more spatially uniform beam. Hence it was easier to get all the infrared power onto the detectors. The final result was better spectra with less effort.
4.1.3 **IR Optics and Detectors**

The infrared optics guided the infrared radiation from the LiIO$_3$ crystal to each of the two detectors. The principal considerations in the design of the optical layout were the reduction of multiple reflections and the minimisation of radiation not striking the detector surface. Figure 4.4 shows the IR optical setup.

A 10cm focal length, broadband anti-reflection (B.B.A.R.) coated, Ge meniscus lens located 9cm after the end of the LiIO$_3$ crystal roughly collimated the infrared beam. Careful alignment of the lens would produce an infrared beam waist of under 2mm, approximately 1m from the collimating lens. This geometry resulted in small spot sizes on both the transmission and normalisation detector lenses. The lens transmitted the infrared radiation but reflected the visible radiation. By facing the convex surface of the collimating lens towards the non-linear crystal, it dispersed the visible radiation after reflection.

The front surface of the normalisation beam splitter divided the infrared radiation into two paths: reflecting to the reference detector and transmitting to the signal detector. Because of the high refractive index ($n=4$) of germanium it reflected approximately $1/3$ of the infrared intensity from the front, uncoated surface of the normalisation beam splitter. The anti-reflection coating on the back
surface reduced the losses through the beam splitter and also reduced the opportunity for radiation from the back surface to be multiply reflected onto a detector. To further reduce the multiply reflected light from making its way onto a detector, the beam splitter was wedged. The 3° wedge angle caused the radiation reflected from the back surface to be totally internally reflected at the front surface. Subsequent reflections were then totally internally reflected by both back and front surfaces until it reached the edge of the beam splitter. Because of the wedge angle the transmitted beam was refracted by 18°.

Each short focal length lens focussed the infrared radiation from the beam splitter onto the respective detector. Germanium was appropriate for such short focal length lenses in order to avoid thick, highly curved CaF₂ lenses. These were again meniscus lenses, with the convex lens surface directed towards the detector to disperse radiation reflected from the detectors.

Cincinnati Electronics Corporation model SDD-7854-S1 InSb infrared detectors were used. We modified the detectors to reduce the problems inherent with multiple reflections off the detector window surfaces by replacing the original sapphire window mounted parallel to the detector surface with a CaF₂ window mounted at Brewster’s angle. This modification made a significant improvement to the overall performance of the system. With the Brewster angled windows, the system became easier to align and had improved baseline spectra.

4.2 VISIBLE OPTICS

Figure 4.5 shows the optical setup of the visible optics. The setup includes the visible lasers used to generate the infrared radiation and the Fabry-Perot etalons used to measure the frequency of the lasers. In this section we discuss the main elements illustrated in this figure.
4.2.1 Pump Lasers

4.2.1.1 Argon Ion Laser

The argon ion, Ar+, gas laser used for the difference frequency generation was a modified Innova 70 small frame laser originally built by Coherent. The modifications to the laser improved its mode structure and frequency stability. A more complete explanation of the modifications can be found in Sinclair (1989) and Forsman (1992). We operated the laser on its green line at 514.677nm (19429.7cm⁻¹).

A temperature-stabilised, concentric etalon in the laser cavity was used to eliminate competing longitudinal modes. Ideally, a concentric etalon is aligned normal to the laser radiation, which is the angle for minimum power loss. However, since this never produced single mode operation, we always adjusted it off axis to properly eliminate competing modes.

A beam splitter located outside the cavity and a few centimetres from the laser output coupler...
directed a small fraction of the beam through a temperature stabilised, 25cm long, Fabry-Perot etalon. The external etalon had two principal functions. During alignment, a piezo electric mount on the output coupler repeatedly ramped the cavity length. This generated transmission peaks that were observed on an oscilloscope. Transmission peaks other than the expected set of smooth, equally spaced peaks indicated the presence of competing modes which cavity alignment would remove. By removing other lines we insured single mode operation. The ability to do this is a distinct advantage over tunable diode laser spectrometers.

After alignment, the laser was locked. To lock the laser, an electronic circuit set the etalon cavity length to correspond to the rising edge of a transmission peak. Using the change in the etalon transmission signal as feedback, the electronics adjusted the output coupler to change the laser cavity length and hence stabilise the output frequency.

These modifications resulted in a single frequency laser with a band width of 1MHz and a drift of only a few MHz per hour. Typically the Ar⁺ laser stayed locked for hours at a time although large noises or vibrations could unlock the laser prematurely. Occasionally the laser would mode-hop, which meant it would unlock and re-lock to an adjacent Fabry-Perot peak. Mode-hops corresponded to sudden jumps in frequency of approximately 300MHz which caused errors in the frequency measurement algorithm, discussed in section 4.2.2.2.1.

### 4.2.1.2 Dye Laser

The dye laser was a Coherent model 699-29 ring laser with *Autoscan*. The laser frequency was tunable over the broad gain region of the rhodamine R6G dye which spans from 565nm(17700cm⁻¹) to 610nm(16000cm⁻¹) but was predominantly run at 583nm. In this section I will discuss only those aspects of the dye laser which impacted on the experiment. For further information, the user's manual describes the design and function of this commercially available unit.

A large frame 20W argon ion laser, lasing at 514.5nm, optically pumped the dye laser. The dye laser performed best when pumped by a single mode Gaussian beam with more than 6.5W. Typical dye laser power under these conditions was approximately 600mW. The frequency jitter of the dye laser when well aligned was measured and found to be on the order of 1MHz (3×10⁻⁵ cm⁻¹).
The tuning of the dye laser requires considerable optical complexity. Several optical elements within the dye laser control the lasing frequency. Three elements contribute a frequency dependent loss mechanism to the round trip path of the laser light. In order from broadest to narrowest frequency dependence they were: a birefringent filter, a thin etalon (FSR=225GHz), and a thick etalon (FSR=10GHz). A tilting plate changed the length of the round trip path length and was the finest means by which the frequency was adjusted.

The Autoscan unit, also manufactured by Coherent, set the dye laser frequency by adjusting its internal optics and using a built-in frequency meter to determine the absolute frequency to within ±200MHz. When Autoscan adjusted the frequency in its feedback controlled mode of operation, it was capable of optimising the internal optics to achieve maximum power. A single externally supplied voltage level controlled the frequency in a purely feed forward manner. This voltage level adjusted the tilting plate, the thick etalon and the thin etalon but did not optimise them for power. As a result, external control could only adjust the dye laser frequency by approximately 1.3cm⁻¹. If the frequency needed to be moved further then Autoscan was required to retune the thick, and thin etalons and birefringent filter.

4.2.1.3 Helium Neon Laser

The purpose of the helium-neon reference laser was to act as a stable 632.8nm(15800cm⁻¹) frequency reference to correct for changes in the length of the Fabry-Perot used to measure frequencies. Our laser, model 105SF, never performed to our expectations but was questionably within the specifications of the manufacturer, Aerotech. They claimed a frequency stability of ±1MHz over 8 hours and ±10MHz over 1 month. They also claim a temperature dependence of 3.6MHz/K.

We often found the laser to be less stable than these claims. Some of the problems were due to reflections feeding back into the laser. Feedback of light into the laser would cause large frequency changes (> 10 MHz) over periods of several minutes. An optical isolator placed before the Fabry-Perot eliminated the feedback from the Fabry-Perot but it occasionally needed realignment. In addition, a red filter located at the laser output prevented scattered light from the other lasers from interfering with the frequency stabilisation. A more general problem was inherent in the design of the
frequency stabilisation technique used internally by the HeNe laser. It did not correct for changes in the ambient temperature or the laser power. Since the laboratory temperature would change by a few degrees over a period of several hours there was an associated frequency drift of the reference laser. Over an even longer time period we suspect that the laser power diminished and caused a long term change in the frequency. This last problem was most important in the time between experimental sessions and was a problem when comparing spectra taken several weeks apart. The laser still served a purpose when comparing spectra taken several days apart.

4.2.2 Frequency Measurement

The system did not actually measure the frequency of the IR radiation directly but calculated it from the difference in measured visible laser frequencies. In fact, only the relative frequencies could be measured, where the term "relative frequency" refers to the frequency relative to a reference determined at the start of each spectral scan. The absolute frequency could only be inferred from the spectra. The difference between the known argon laser frequency, 514.677nm (19429.7cm\(^{-1}\)), and the dye laser frequency as measured by "Autoscan" would determine the frequency to within 200MHz (7\(\times\)10\(^{-3}\)cm\(^{-1}\)). Then using the tabulated spectral line frequencies as given in Hitran96 (Rothman et al., 1992a) the spectral feature of interest could be identified.

The next section describes the system which was responsible for the frequency measurements. The technique was based on the measurement of transmission peaks through a confocal Fabry-Perot etalon. Good frequency measurements were vital to the line shape analyses, and a detailed knowledge of the frequency measurement process allowed for a correct interpretation of its precision and accuracy. The possible sources of error will be discussed along with possible methods of correction.

4.2.2.1 Frequency Measurement Using a Confocal Fabry-Perot Etalon

The frequency measurement subsystem, whose principal component was a temperature stabilised, 25cm, confocal Fabry-Perot etalon, determined the relative frequencies of both the dye and Argon ion lasers. A series of mirrors and beam splitters directed the dye laser, Argon ion laser, and HeNe laser beams through the Fabry-Perot collinearly. An applied ramp voltage to the piezo electric
transducer, PZT, mount of the Fabry-Perot output mirror ramped the Fabry-Perot's length approximately 0.6μm at a frequency of 8Hz. Since a transmission peak occurs whenever the length of the cavity is an integer number of quarter wavelengths, 0.6μm nominally corresponded to four transmission peaks for each laser in every ramp cycle.

After the Fabry-Perot a red filter and a diffraction grating separated the overlapped beams into the original three components and directed them onto three separate photodiodes. Ramping the Fabry-Perot cavity length generated a set of transmission peaks for each laser beam. The ramp voltages at which transmission peaks occurred determined the relative frequencies of each laser. The HeNe reference laser was assumed constant and the data acquisition software used the change in ramp voltage for the HeNe transmission peaks to correct for thermal changes of the Fabry-Perot length.

If the laser frequencies and the cavity ramp were stable, the peaks for a particular laser would always occur at the same ramp voltage. If a laser changed frequency by a small amount, then the corresponding transmission peaks also shifted slightly. The change in transmission peak voltage was a measure of relative frequency. The free spectral range, FSR, related the change in transmission peak voltage to an actual frequency change since the frequency difference between two successive transmission peaks of a Fabry-Perot etalon corresponds to one free spectral range. The free spectral range of a confocal etalon is related to its length, \(L\), through

\[
\nu_{\text{fsr}} = \frac{c}{4nL}
\]

where \(n\) is the index of refraction of the gas inside the etalon. Forsman measured the length of this Fabry-Perot using a travelling microscope (Forsman, 1992) and found a free spectral range of 301.69±0.12MHz (1.0063(4)×10^{-2}cm^{-1})\(^{11}\).

The frequency measuring technique was as follows. Let \(V_n^l\) be the input voltage to the ramp corresponding to transmission peak \(n\) of laser \(l\). The relative frequency, \(\nu'\), was defined by,

\[
\nu' = \left(\frac{V_2^l}{V_2^l - V_1^l}\right)\nu_{\text{fsr}} + m\nu_{\text{fsr}}
\]

\(^{11}\)Although this was the free spectral range used by the data acquisition program it was not the free spectral range used for most of the data analysis. For a further discussion see section 5.3.1.
where \( m \) is the order number and the quantity in brackets is referred to as the fractional fringe. At the start of each scan, \( m \) was initialised to zero. The acquisition algorithm always assumed that the laser frequencies changed in small positive incremental steps of less than one FSR. A fractional fringe change of more than one increased the order number by one. Because the laser frequency could change by more than one free spectral range there was some ambiguity about the assignment of the order number unless the lasers were guaranteed to move much less than one fringe for each step.

Equation 4.9 assumes that the cavity length at the beginning of each ramp cycle remained constant. However the cavity length did change due to small fluctuations in the temperature of the Fabry-Perot. As a means of correcting for the thermal drifts the second transmission peak of the HeNe reference laser was used as a fiducial mark. Thus, equation 4.10,

\[
\tilde{\nu}' = \left( \frac{\nu_2^l - \nu_2^{ref}}{\nu_2^l - \nu_1^l} \right) \tilde{\nu}_{far} + m \tilde{\nu}_{far}
\]  

(4.10)

determined the thermally compensated frequencies of the dye and Argon ion lasers, and equation 4.9 was only used for the reference laser. The quantity in brackets is again referred to as the fractional fringe.

The data acquisition program, known as Spect33, automated the entire frequency measurement process. Both before and after the acquisition of each data point, Spect33 measured the positions of the transmission peaks as a function of ramp voltage. The acquisition program wrote the relative frequencies of all three lasers to the output file. The random error in the frequency measurements diminished as the square root of the number of times the peaks were measured. As a compromise between time and precision, the peaks were usually sampled five times before and five times after each data point which took approximately one second in total.

An additional source of inaccuracy was the non-linearity of the ramped distance of the PZT versus ramp voltage. This non-linearity was corrected by applying a quadratic correction to the transmission peak positions (Forsman, 1992).

**4.2.2.2 Corrections to Frequency Measurements**
The preceding section described the operation of the frequency measurement system under several assumptions. The following sections discuss possible errors in the frequency measurements when one or more of these assumptions breaks down. Under some conditions I corrected the frequency data, but more frequently I ignored small errors (<2MHz) and discarded spectra with large errors.

### 4.2.2.2.1 Frequency Changes Greater than 301MHz

If a laser frequency changed by one or more free spectral ranges (i.e. >301MHz) in a single step, Spect33 would make an error in incrementing the order number, \( m \). The relative frequency measurement of that laser would then be in error by an integer number of free spectral ranges and any subsequent frequency measurements would be subject to the same error. In a spectral region where transmission changed rapidly, this type of error was obvious; it appeared as a discontinuity in the spectral feature. If we noticed this discontinuity, we repeated the spectra. Otherwise errors in the frequency axis were not noticed until analysed. We were usually able to correct the data unambiguously by adding or subtracting an integer number of free spectral ranges to the affected data, where \( \nu_{fr} = 301.69 \text{MHz} \). If this proved ambiguous or impossible the spectrum was discarded. In practice, this type of error only occurred occasionally.

### 4.2.2.2 Reference Laser Drift

It was anticipated that the HeNe reference laser would be stable to within several mega-Hertz over a period spanning several months. In reality, the laser performed far short of these expectations and drifted over time scales as short as several hours.

Any change in the reference laser frequency resulted in frequency measurement error because Spect33 used the reference laser to correct for changes in the Fabry-Perot length. Drifts of the reference laser were naturally interpreted as changes in dye and Argon laser frequencies. Assuming a reference laser drift of \( \Delta \nu^{ref} \), equations (4.9) and (4.10) relate the recorded change in the dye and Argon laser frequencies, \( \Delta \nu^d \), to the reference drift. Combining equations (4.9) and (4.10) one finds the following relation
\[ \Delta \tilde{\nu}^l = \frac{V_2^{\text{ref}} - V_1^{\text{ref}}}{V_2^l - V_1^l} \Delta \tilde{\nu}^{\text{ref}} = \frac{\lambda^{\text{ref}} - \lambda^l}{\lambda^l} \Delta \tilde{\nu}^{\text{ref}}. \]  

Fortunately, since the infrared frequency is equal to the small difference of the dye and Argon laser frequencies the effect is reduced by approximately a factor of ten as shown in the following equation:

\[ \Delta \tilde{\nu}^{IR} = \Delta \tilde{\nu}^{\text{ref}} - \Delta \tilde{\nu}^{\text{dye}} = \frac{\tilde{\nu}^{\text{ref}} - \tilde{\nu}^{\text{dye}}}{\Delta \tilde{\nu}^{\text{ref}}}. \]  

Thus spectra with a reference laser drift of even 10 MHz over the scan were acceptable since such a drift would correspond to only one MHz in the infrared. In principle one could remove the effects of the reference laser drifting during a scan using equation 4.12. Assuming the Fabry-Perot cavity length had not changed since the beginning of the scan, the difference between the recorded reference laser frequency at each point and the first point gives the reference laser drift, \( \Delta \tilde{\nu}^{\text{ref}} \). Such corrections were never implemented. A more serious problem occurred if the laser drift resulted in a change of its fringe order number.

4.2.2.2.3 Reference Laser Order Number Change

An error would also occur if the fringes of the reference laser drifted such that a change in fiducial peak order number occurred while taking a spectrum. Such a change could occur due to drifts of the reference laser or the Fabry-Perot. Unlike the reference laser drift of the previous section this problem affects both lasers' apparent frequencies. The correction for order number was given by,

\[ \Delta \tilde{\nu}^{IR} = \frac{\tilde{\nu}^{\text{ref}} - \tilde{\nu}^{\text{dye}}}{\Delta m \tilde{\nu}^{\text{ref}}}. \]  

For an IR frequency of 2077 cm\(^{-1}\) the correction is \( \Delta m \times 39.65 \) MHz \( (1.323 \times 10^3 \) cm\(^{-1}\)).

4.2.2.3 Spectrum to Spectrum Inter-Comparison

Despite the fact that each spectrum would start at a different frequency, it was possible to inter-compare the relative frequencies of different spectra. If the reference laser was stable, the measured frequencies only needed to be adjusted by an integer number of free spectral ranges as described above. A change in reference laser order number (plus or minus one) could also be
corrected. Because the reference laser did drift with time, inter-comparison of spectra could only be done reliably between spectra taken within a few days of each other.

To improve matters, I suggest using a reference laser with better long-term stability. In order not to compromise the frequency measurements with the short-term reference laser drifts, measurement of the laser frequency should be taken only at the start of a spectral run but not during the run.

4.3 SIGNAL PROCESSING and SOFTWARE

The signal processing chain consisted of those components involved with the processing of electrical signals before acquisition by the system computer. Figure 4.6 schematically shows the progression of signals from the IR detectors and the frequency measuring system to the computer interface.

The precise measurement of the very weak infrared signal was made possible by using phase sensitive detection. An acousto-optic modulator modulated the Ar+ laser, which in turn caused the infrared signal to be modulated. A signal generator produced a sinusoidal modulation waveform which drove the acoustic-optic modulator and also provided the reference signal to two lock-in amplifiers. Because the optical modulation occurs at twice the frequency of the modulation waveform, the 40kHz modulation waveform modulated the light Ar+ laser beam at 80kHz.

The lock-in amplifiers were Stanford Research Systems SR510's operated in 2f mode with the "dynamic range" set to "low". The zero offset and scale settings of each lock-in were set such that zero to full signal gave as large an output variation as possible. This was done to take full...
advantage of the 12 bit converter. A simple $\times 0.1$ voltage divider circuit reduced the analog output of each lock-in from (-10V to +10V) to (-1V to +1V) before the signals went to the analog-to-digital converter, ADC.

The frequency and infrared signals were fed through the 16 channel multiplexer which in turn fed the 12 bit ADC. The channel used for the normalisation signal had a sample and hold circuit. Reading the transmission channel initiated a sample and hold on the normalisation channel. Normalisation could then be performed using simultaneous transmission and normalisation measurements.

The data acquisition program, Spect33, automated the data acquisition process for the experiment. The program was originally developed by Jon Forsman, but numerous people, including myself, have made contributions since. The next few paragraphs will outline the operation of Spect33.

Before entering the Spect33 program, the operator must set the dye laser frequency using
Autoscan software. This process optimised the thick etalon, thin etalon and birefringent filter for a particular operating frequency. Once running, Spect33 controlled the dye frequency by changing only a single voltage. Setting the scan description, which contained the necessary parameters controlling the taking of data, was the first step in running a spectrum. Of note were the parameters controlling the frequency width of the scan, the nominal frequency separation of the data points, the number of samples per data point, the time interval between samples, and the variable frequency spacing of data points.

The acquisition of each spectrum started with the zeroing of the infrared detectors. A remotely controlled shutter blocked the dye laser beam while Spect33 recorded the zero offset of both detectors. This correctly accounted for any inherent offset of the detector or ADC and also accounted for any offset caused by stray modulated light from the Ar* laser striking the detector. Based on the signal levels, Spect33 chose an arbitrary scaling factor with which it multiplied the signals\(^\text{12}\).

At the start of a spectrum, Spect33 set the dye laser to correspond to the nominal starting frequency and advanced by set increments. The scan description specified a frequency increment but this was multiplied by \((1+r|\delta \tau/\delta \delta|)\), where \(\delta \tau\) was the change in transmission during the last frequency interval \(\delta \delta\), and \(r\) was a multiplier set in scan description. This variable spacing allowed for more data points in spectral regions of rapidly changing transmission.

Half the total number of Fabry-Perot traces were acquired before and the other half after each data point. For each trace a simple algorithm identified and determined the locations of the Fabry-Perot transmission peaks for each laser. Spect33 then used equations 4.9 and 4.10 to determine the relative frequency of the each laser for each Fabry-Perot trace. The mean frequency determined from all the Fabry-Perot traces was recorded as the measured frequency for each laser.

\(^{12}\text{This factor was an unfortunate program relic but was easily removed from the data.}\)
Each data point was the average of a set number of samples. For each sample the algorithm divided the normalisation signal by the transmission signal to give the normalised transmission. The mean and variance of the normalised transmission was calculated for the set of samples and formed one data point. An alternative normalisation scheme would first calculate the mean of the transmission and normalisation signals separately and then ratio the means. Appendix I shows that the first method, used in Spect33, may not be correct and may lead to a systematic over-estimation of the normalised signal. However in practice, examination of actual data showed that the first method produced a systematic transmission signal only $3.0(0.2) \times 10^{-5}$ larger than the second method. The actual method of normalisation was therefore irrelevant.

4.4 GAS HANDLING

The gas handling system controlled the composition, pressure, and temperature of the gas sample being studied. Figure 4.7 shows the main features of the system.

The sample cell was a simple design: a thin walled aluminum tube with relatively massive aluminum end caps. Mounting the calcium fluoride windows at Brewster’s angle minimised reflections.
from the gas-window interfaces, thus reducing problems inherent with multiple reflections. A machined aperture was attached to each end of the cell in such a way that it could be rotated in and out of the beam path. When positioned in the beam path, these apertures helped to align the cell such that the infrared beam travelled precisely down the centre.

There were three 1/4 inch ports: ports A and B were located at one end of the cell, and port C at the other end. The gas entered through port A and was evacuated through port C. This configuration allowed gases to be changed efficiently since most of the volume could be flushed through. A MKS model 120AA high accuracy pressure transducer measured the sample pressure through port B. A 3/8 inch copper tube connected a small turbo pump to port C. The fairly straight and short length of tubing allowed the cell to be evacuated in less than 5 minutes. The 120AA was calibrated up to 100kPa to be accurate to within 0.05% of the reading.

To check for leaks, the cell was evacuated, after which all the valves were closed. The pressure of the cell rose less than 0.03kPa over a 12 hour period. Additionally, pressures measured at the beginning and end of scans never showed any systematic differences. These tests assured that cell leaks were not a problem.

The cell was temperature controlled to ensure a uniform and controlled gas temperature. A resistive heating wire contained in an external spiral groove heated the cell. Wound over the heating wire, a layer of fibre glass tape insulated the cell. A small thermistor, glued one quarter of the length from one end, supplied temperature feedback to a computer dedicated to controlling the cell temperature. The computer controlled the duty cycle of the heating wire such that the thermistor resistance corresponded to the desired set temperature. This technique maintained the thermistor temperature to within a small fraction of a degree.

The cell temperature was measured using a thermocouple mounted midway along the cell. The uniformity of the cell temperature was occasionally measured using a wand thermocouple probe. As expected, the cell tended to be warmest in the middle and cooler towards both ends. With the heating system described above, the temperature difference between the cell centre and ends was between 0.5K and 1.0K for a midpoint temperature of 301K. To improve the temperature distribution, a length of heating tape was added to each end of the cell. A fixed voltage applied to the heating tapes reduced
the temperature variation to less than 0.5K. By mounting the feedback thermistor one quarter of the way along the cell length, it effectively controlled the mean cell temperature.

Each gas cylinder supplied gas at about 20psi gauge pressure through a 1/8 inch stainless steel tube. I performed many of the earlier experiments using lengths of 1/4 inch Teflon tubing up to 7 metres in length. Unfortunately, Teflon tubing is surprisingly permeable (Blanchard, 1996). As a result many of the earlier experiments were contaminated with air in the cell. The analysis section will discuss this problem further. The pure CO$_2$ was Matheson *aquarator* grade of at least 99.99% purity and less than 7ppm CO.

### 4.5 METHODOLOGY

With most improvements in the experimental set-up, there followed an associated change in the experimental methodology. The analysis of each experimental session would often expose new, until then unnoticed, sources of uncertainty (or noise). These newly found sources of uncertainty often required changes to both apparatus and methodology. For example: initially there was a preoccupation with maximising the infrared power. The quest for power required much time to be spent maximising the power output of the Ar$^+$ and dye lasers. We discovered, however, that the quality of the signal normalisation and the precision of frequency measurements had a larger impact on the quality of the data than the total IR power. As a result, the experimental emphasis turned from concentrating on raw IR power to time spent improving the normalisation.

#### 4.5.1 System Setup

The first step in preparing the infrared system was to direct and focus the visible laser beams such that they were collinear within the crystal and that the beam waists were of appropriate size. A beam profiler measured the size and shape of the visible beam waists and a pair of quadrant detectors ensured collinearity of the visible beams. An iterative alignment process of adjusting the visible beam pointing and the infrared optics eventually maximised the power on the detectors. In a well aligned system, the detectors displayed a characteristic behaviour; small horizontal or vertical movements of the detectors caused little change in the incident power until the beam reached the edge of the
detector and then the power dropped off rapidly. This indicated that the beam was smaller than the detector and was well centred on the detectors.

An experimental session usually required several weeks of work to completely align the infrared optics. After the initial alignment, the optics usually required only slight adjustments each day.

Several quick spectra were taken to ensure that the feature of interest fell within the scan range and if necessary *Autoscan* was used to adjust the dye laser frequency. Next, baseline spectra were taken iteratively with optical adjustments to reduce variation in the baseline over the spectral scan. Sinusoidal baseline structure was usually the signature of weak interference between multiply reflected beams. These effects were eliminated mostly on a trial and error basis. Common sources were the focussing lenses in front of the detectors. Slightly angling these lenses and the detectors usually corrected the problem. The change to Brewster angled detector windows dramatically reduced multiple reflections which were otherwise a primary source of normalisation problems. Once the flat baselines were established, we were ready to take spectra.

### 4.5.2 Recording Spectra

During the setup phase, optimisation could reduce the normalised drift across a 1.3 cm\(^{-1}\) baseline scan to less than one part in one thousand. Even so, we took baseline spectra regularly as part of the operating methodology for two reasons. Most importantly, the baseline spectra verified that the system performance did not degrade. Additionally, the slow, frequency-dependent drifts that appeared in the baseline spectra were repeatable and therefore could be subtracted from the transmission spectra. When alternating between transmission spectra and baseline spectra there were two considerations: minimising the time spent pumping and filling the cell, and assuring each transmission spectrum was taken temporally close to a baseline spectrum. The preferred cycle occurred in sets of four scans; a baseline spectrum preceded and followed each pair of transmission spectra. Since each transmission scan was either preceded or followed by a baseline there was always a baseline taken as closely in time as possible. It also meant that two transmission spectra could be taken with only one evacuation of the cell. This cycle resulted in two baseline spectra being taken in
sequence. Any adjustments that might affect the normalisation, such as peaking a laser, took place between these baseline spectra.

![Figure 4.8. Ordering of data taking and experimental adjustments.](image)

To prepare the sample cell for a baseline scan, the pump evacuated the cell. It was then flushed with several 10 kPa fills of helium before final evacuation. Even during the baseline scan, the pump continued to evacuate the cell and the main valve was left open to evacuate the small volume in the tee between the valves. Using this technique, I never found evidence of CO$_2$ in the baseline spectra and at the end of the baseline scans, the cell was ready to fill with pure CO$_2$.

The signals were over-sampled since the time constant on the lock-in amplifier was set to 10ms whereas it was sampled every 3ms. Over-sampling reduced the random error from the ADC by increasing the number of samples taken. Over-sampling required correction of the error estimates given by the Spect33 since consecutive samples were to some extent correlated. Typically spectra were taken with 400 samples per point. Because the baseline spectra contained little structure, the frequency information was not as important as it was for CO$_2$ spectra. Hence, for baselines more time was spent averaging the signal and less time taking frequency data. For baseline spectra we typically took 50 frequency points and 1000 points averaged per sample.

Spectra were taken at many different pressures, but for two particular pairs of spectra (CO2Q2793 + CO2Q2794 and CO2Q2799 + CO2Q2800)$^{13}$ the gas in the cell was retained while the frequency was changed. This ensured that the pressure for the two runs at different frequencies was identical and allowed the paired spectra to be spliced together.

As much as possible, adjustments to the system during operation were minimised so as not to change the order number of the frequency-measuring etalon. The Ar$^+$ laser power would usually

$^{13}$These are the filenames of the spectra. Appendix II contains a complete list of other spectra taken.
decay on a time scale of a few hours but it was possible to peak the laser for power while it remained locked. If the system was run during the late evening and night, it was particularly stable.
CHAPTER 5

FIRST ORDER LINE MIXING

The experimental spectra have been divided into three broad categories, low pressure (0 to 1.4kPa), medium pressure (1.4 to 11kPa), and high pressure (11 to 70kPa). These divisions follow quite naturally from a consideration of the mechanisms governing the line shape. For each pressure region the method of analysis and the quantities that could be extracted were different. Figure 5.1 shows a representative spectrum from each of the three pressure regions. The edges of the regimes are not as abrupt as we have described them, but experience fitting the spectra naturally led to such divisions.

Figure 5.1. A representative experimental transmission spectrum from each of the three pressure regions: low, medium, and high.
In this chapter we present spectra of the $v_1+v_2 Q$-branch in CO$_2$ at pressures below 11kPa, i.e. low and medium pressures. At these pressures, we have assumed that line mixing is linear in pressure and may be analysed using the first order Rosenkranz approximation. The theory of chapter 2 did not include the treatment of the translational motion (see section 2.2.1). We begin this chapter with a discussion of how we incorporate the effects of molecular motion into the line mixing formalism.

5.1 INCLUDING TRANSLATIONAL LINE SHAPE EFFECTS

The line mixing line shape discussed in the Theory chapter ignored the translational effects of the molecule; equation 2.15 represents line mixing effects in what is essentially a Lorentzian line shape model. At high pressures, ignoring translational effects can be a reasonable approximation, since the effects are small relative to the large collision broadened line widths. However, for gas pressures below 11kPa the contribution from translational effects is substantial. Here we will develop a line shape that includes translational effects on a line-by-line basis.

The translational motion of the absorbing molecule causes a Doppler shift of the radiation frequency, in the molecule’s frame, which is proportional to the molecular velocity in the direction of propagation. This is an inhomogeneous effect, dependent on the molecular velocity, which if integrated over the distribution of velocities, leads to a Gaussian line shape. The Doppler line shape is characterised by the $1/e$ point, $\alpha_D$, and is given by,

$$ I(v) = \frac{1}{\alpha_D \sqrt{\pi}} e^{-\left(\frac{v-v_0}{\alpha_D}\right)^2}, $$ (5.1)

where $\alpha_D$ is given by,

$$ \alpha_D = \left(\frac{v_0}{c}\right)\left(\frac{2k_B T}{m}\right)^{0.5}. $$ (5.2)

The Voigt line shape is the convolution of the Lorentzian and Gaussian line shapes and is the simplest line shape combining collisional and translational effects. The Voigt line shape assumes the two effects are uncorrelated, that is the collisions do not affect the translational line shape. A common
method of calculating the Voigt profile is to use the complex probability function, $w(x,y)$, defined by,

$$w(x,y) = \frac{i}{\pi} \int_{-\infty}^{\infty} \frac{e^{-t^2} dt}{x + iy - t}.$$  \hspace{1cm} (5.3)

In terms of the complex probability function, the Voigt profile (Humlíček, 1979) can be written as,

$$I(v) = \frac{1}{\sqrt{\pi} \alpha_D} \text{Re} \left[ w \left( \frac{v-v_0}{\alpha_D}, \frac{\gamma}{\alpha_D} \right) \right].$$  \hspace{1cm} (5.4)

But collisions do affect the translational line shape as was first pointed out by Dicke (1953). Velocity-changing collisions change the direction of travel of the molecule. Such collisions may or may not also be phase-changing collisions. Velocity-changing collisions tend to localise the molecule and the motion of the molecule goes from free streaming at zero pressure towards diffusional at higher pressures. The effect reduces the Doppler contribution to the line-width and hence is called Dicke narrowing. Increasing pressure increases the velocity-changing collision frequency which in turn further reduces the line-width.

There are two common line shape models which include Doppler broadening and Dicke narrowing. The models make different assumptions about the nature of the collisions and are known as the soft collision (Galatry, 1961) and the hard collision (Nelkin and Gatak, 1964) models. Varghese and Hanson (1984) review both these models.

The soft collision model developed by Galatry (1961) incorporates Dicke narrowing into the line shape profile using a diffusional model. In this model, a molecule’s motion, described by a diffusional process, is completely uncorrelated with itself after many infinitesimally small, velocity-changing collisions. If we ignore phase-changing collisions we can calculate the autocorrelation function due only to translation. The reciprocal of the correlation decay time defines an “effective velocity-changing collision rate”. The model is then expressed as the Fourier transform of the product of this translational autocorrelation function and the time domain representation of the Lorentz line shape. Since we interpret the diffusional process as consisting of many small or soft collisions, this model most accurately corresponds to the case where the active molecules are much more massive.
than the perturbing molecules. Such a system is CO in He which has been studied by Duggan et al. (1993; 1995).

In the soft collision model, the velocity-changing collision rate is parametrised by a quantity known as the friction constant, $\beta$, related to the mass diffusion constant, $D$, by $\beta = k_b T/mD$. We will use an alternative quantity referred to as the narrowing parameter, $z = \beta/k\bar{v}$, where $k$ is the radiation wavenumber and $\bar{v}$ is the most probable speed of the active molecule, $\bar{v} = \sqrt{2k_bT/m}$. Because $D$ is inversely proportional to pressure, $z$ should be proportional to pressure.

The hard collision model developed by Nelkin and Gatak (1964) and later adopted by Rautian and Sobel'man (1967) assumes that each collision is a hard collision which redistributes the active molecule into a thermal distribution. This amounts to a relaxation of the molecular motion towards a thermal distribution. This single translational relaxation rate, $\beta$, determines the extent of Dicke narrowing. The pressure-broadened line width is governed by the phase-changing relaxation rate, $\Gamma$.

In the time domain, the hard collision and soft collision models have the same short and long time behaviours. At short times the models are free streaming and at long times they are both diffusional. Hence, at long times the hard collision parameter $\beta$ can also be related to the diffusion constant and we define the narrowing parameter, $z = \beta/k\bar{v}$, for the hard collision model as well.

Neither the hard- nor soft-collision models completely describes the translational motion of the molecule. However, the actual differences between the two line shapes are very small (see for example Pine, 1994). Studies of CO show, for roughly equal active-to-perturber mass ratios, that the two models fit the experimental spectra equally well (Duggan et al., 1993). We expect the same to be true for pure CO$_2$ which has equal active and perturber masses. The soft collision model requires a numerical Fourier transform of the time domain autocorrelation function whereas the hard collision line shape, like the Voigt model, can be expressed in terms of the complex probability function. Because the hard collision model is both easier and faster to compute, we have chosen to use the hard collision model as a basis for the spectral analysis.

Although we do not explicitly perform the convolution, the final line shape can be best understood as the convolution of the hard collision translational line shape with the Lorentz plus dispersion line shape of equation 2.15. We will start in the time domain since a frequency domain...
convolution is a simple product in the time domain. A line shape which is symmetric about a central frequency and positive everywhere requires that the autocorrelation function is real and symmetric about zero time, $\Phi(t)=\Phi(-t)$. This even symmetry allows equation 2.4 to be re-written as the real part of an integral from 0 to $\infty$:

$$k(\omega)_{sym} = \frac{1}{\pi} \text{Re} \left[ \int_0^{\infty} \Phi(t) e^{i\omega t} dt \right]. \tag{5.5}$$

It has been noted (but not proven) by several authors (Lavorel et al., 1990b; Strow et al., 1994) that the asymmetric line mixing contribution to a line shape is given by the imaginary part of this same equation. In other words, the asymmetric line mixing contribution can be found from the time domain representation for any symmetric line shape, such as the hard collision line shape. The total normalised line shape is then given as,

$$I(\omega) = \frac{1}{\pi} \text{Re} \left[ \int_0^{\infty} \Phi(t) e^{i\omega t} dt \right] + \frac{Y}{\pi} \text{Im} \left[ \int_0^{\infty} \Phi(t) e^{i\omega t} dt \right] \tag{5.6}$$

where $Y=q/p$ is the size of the line mixing component relative to the symmetric component. Lavorel et al. (1990b) justify this equation with a single sentence, "Such an extension is straightforward, since the dispersive profile is merely obtained from the imaginary part of the e.m. field autocorrelation function (instead of the real part of the Lorentz profile)." Although I am not aware of a general proof for this equation, it can be shown true for a Lorentz line shape by straightforward substitution of the Lorentz autocorrelation function, $\Phi(t)=e^{-\Gamma|t|}$, where $\Gamma$ is the phase-changing relaxation rate.

---

14 Although we show this approach to be correct here, we will suggest in the next chapter on speed dependence, that equation 5.6 is not correct in general. In particular it is incorrect for a speed-dependent profile.

15 We will follow the convention and use the symbol \(\Gamma\) for both the Lorentz line width in rad/sec and the phase-changing relaxation rate in sec^{-1}. This is done because the two quantities are numerically equivalent within both the Lorentz and hard collision models.
in sec\(^{-1}\). Given that equation 5.6 is true for a Lorentz line shape, it is also valid for \(\Phi(t) = \psi(t)e^{-\Gamma t}\), where \(\psi(t)\) is any real (and therefore symmetric) autocorrelation function. Thus, equation 5.6 represents the convolution of the Lorentz and dispersion line shapes with any other symmetric line shape (such as that due to the translational motion).

Now we look at the hard collision model in particular. Equation 6.2 of Rautian and Sobel'man (1967) represents the uncorrelated hard collision line shape without line mixing:

\[
I(\omega) = \frac{1}{\pi} \text{Re} \left\{ \int \frac{W_M(\nu)\,d\nu}{\Gamma(\nu) + \beta - i\left(\omega - \delta(\nu) - k\cdot\nu\right)} \right\}, \quad (5.7)
\]

where \(\beta\) is the velocity relaxation rate (sec\(^{-1}\)), \(\Gamma(\nu)\) is the phase changing relaxation rate (sec \(^{-1}\)), \(W_M(\nu)\) is the equilibrium velocity distribution, \(\delta(\nu)\) is the line shift (rad/sec), \(k\) is the wave vector along the direction of propagation, \(\nu\) is the molecular speed and \(\nu\) is the molecular velocity. Rautian and Sobel'man show that if \(\Gamma(\nu)\) and \(\delta(\nu)\) are independent of velocity then equation 5.7 can be rewritten as the convolution of a Lorentzian line shape and a symmetric translational line shape,

\[
I(\omega) = \frac{1}{\pi} \int \text{Re} \left\{ \frac{1}{\Gamma - i(\omega - \delta - \omega')} \right\} \text{Re} \left\{ \frac{1}{\beta - i(\nu' - k\cdot\nu)} \right\} \frac{W_M(\nu)\,d\nu}{\Gamma(\nu)} \, d\omega'. \quad (5.8)
\]

Although this equation is not a time domain representation, from the development of Rautian and Sobel'man it can be shown to be equivalent to a time domain form. As stated before, the fact that equation 5.7 can be written in this form means that the line mixing component of the line shape can be determined from the imaginary part of the term within the braces of equation 5.7. Using a Maxwellian distribution for \(W_M(\nu)\) and assuming that \(\Gamma(\nu)\) and \(\delta(\nu)\) are independent of speed, the integrals in equation 5.7 can be related to the computationally efficient complex probability function as follows:
Chapter 5: FIRST ORDER LINE MIXING - Including Translation Effects

\[ \int \frac{W_M(v) dv}{\Gamma + \beta - i(\omega - \delta - k\bar{v})} = \sqrt{\pi} \frac{\omega - \delta}{\omega_D} \left( \frac{\omega + \beta}{\omega_D}, \frac{\omega_D}{\omega_D} \right). \] (5.9)

The Doppler width in rad/sec, \( \omega_D \), has been used since \( \omega_D = k\bar{v} \).

Thus, the hard collision line shape with mixing is given by

\[ I(\omega) = \frac{1}{\sqrt{\pi} \omega_D} \left[ \text{Re} \left\{ \frac{\omega}{\omega_D} \left( \frac{\omega + \beta}{\omega_D} \right) \right\} + Y \text{Im}\{...\} \right]. \] (5.10)

The rates \( \beta \) and \( \Gamma \) are in units of sec\(^{-1}\) but the frequencies \( \omega \) and \( \omega_D \) are in units of rad/sec. To avoid confusion we explicitly re-write this equation in frequency units of Hz or cm\(^{-1}\),

\[ I(v) = \frac{1}{\sqrt{\pi} v_D} \left[ \text{Re} \left\{ \frac{v}{v_D} \left( \frac{v + z}{v_D} \right) \right\} + Y \text{Im}\{...\} \right]. \] (5.11)

We have substituted the dimensionless narrowing parameter, \( z = \beta/k\bar{v} \), for the velocity relaxation rate. Note that because these line shapes are both normalised, \( I(v) = 2\pi I(\omega) \).

In summary, we used the hard collision model and added the line mixing contribution using equation 5.6. The first term in equation 5.11 represents the usual hard collision model while the second term represents the dispersion line shape convolved with the hard collision translational line shape.

For computational purposes we simplified equation 5.11 using substitutions similar to those suggested by Nelkin and Ghatak (1964):

\[ I(v) = \frac{1}{\pi v_D} \frac{U(1 - zU) - zV^2 + YV}{(1 - zU)^2 + z^2V^2} \] (5.12)

where,
Chapter 5: FIRST ORDER LINE MIXING - Including Translation Effects

\[ U(v,\gamma,z) = \sqrt{\pi} \, \text{Re} \left[ w \left( \frac{v}{v_D}, \frac{\gamma}{v_D}, +z \right) \right] \]  \hspace{1cm} (5.13)

\[ V(v,\gamma,z) = \sqrt{\pi} \, \text{Im} \left[ w \left( \frac{v}{v_D}, \frac{\gamma}{v_D}, +z \right) \right] . \]  \hspace{1cm} (5.14)

This was the form used for implementing the hard collision model with line mixing into the spectral analysis program which will be described later. The last term, \( V \), contributes the asymmetrical, line mixing component to the line shape. Note that setting \( z = 0 \) in equation 5.12 removes Dicke narrowing effects from the line shape and leaves the simpler Voigt model with an asymmetry component. It can also be shown that equation 5.12 approaches a Lorentz line shape with a dispersion component as \( z \to \infty \). Because the model only requires a single calculation of the complex probability function, it will evaluate almost as quickly as a Voigt model.

This line shape model has been published by Berman et al. (1997) but the same model was simultaneously published by Pine (1997a). Pine's development is quite different although his final form is identical to equation 5.10.

5.2 SPECTRAL FITTING: Line-Fit

The fitting program, written to analyse spectra, was called Line-Fit. Line-Fit was capable of fitting a variety of line shape models to multi-line experimental spectra by optimising a number of adjustable line shape parameters. By fitting spectra we mean minimising the difference, in a least squares sense, between the experimental transmission spectrum and the calculated transmission spectrum. I wrote all parts of this program with the exception of the Levenberg Marquardt algorithm and the complex probability function; both of which are discussed later. The program was written in Borland C++ version 3.1.

As stated, the experimental spectra were transmission spectra, \( i.e. \) energy through the cell normalised to the input power. We also took baseline spectra with no gas in the cell to determine the 100\% transmission level. Line-Fit calculated the normalised transmission spectrum, \( \tau (0 < \tau < 1) \), using the ratio,
\[
\tau = \frac{\text{transmission spectrum}}{\text{baseline spectrum}} \tag{5.15}
\]

Within the noise levels of the spectrum, the ideal baseline spectrum is indistinguishable from a horizontal line, but because our signal-to-noise levels were as high as 4000:1, structure in the baseline spectra was extremely difficult to eliminate. Variations in the baseline spectrum alone had always been less than 1 part in 200 but more recently was improved to better than 1 part in 1000. This improvement resulted from the change to an elliptical beam geometry and to detector windows mounted at Brewster’s angle (see the Experimental section).

Originally, the baseline spectra contained repeatable, frequency-dependent structures. To account for the structure, the baseline spectra were not smoothed but linearly interpolated to the frequencies of the transmission spectra. In contrast, baseline spectra taken with the newer system showed only marginal structure and tended to be slowly varying functions of frequency, on which more rapidly varying non-repeatable fluctuations were superimposed. To minimise the unnecessary

---

Figure 5.2. Sample baseline spectrum with a 3rd order Chebychev polynomial fit.
addition of random noise to the transmission spectra, a 3rd order Chebychev polynomial fit (Press et al., 1992) was performed. Figure 5.2 shows a baseline spectrum from the most recent experimental configuration.

The transmission is related to the line shape absorption coefficient, $k(v)$, through $\tau(v) = B e^{-Lk(v)}$, where $B$ is the baseline offset. We refer to $B$ as an offset because of its significance to the absorption coefficient, $k(v) = -\ln(\tau(v))/L + \ln(B)/L$. Ideally $B$ would equal unity but in order to allow for experimental error it was included as an additional fit parameter. It also accounted for the wings of lines not explicitly included in the analysis since it was found using a general line-by-line program that the wings of these lines summed to give an approximately uniform absorption over the region of interest.

With each experimental point, an uncertainty estimate based on the variance of the sampled signal was recorded (see the Experimental section). These uncertainty measurements were scaled by the same baseline spectrum as the transmission spectrum. Thus each normalised transmission point, $\tau_b$, had associated uncertainty $\Delta \tau_b$. 

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The analysis also accounted for an uncertainty associated with the frequency measurements. Frequency measurement errors were most serious when the transmission varied rapidly with frequency. Under this condition, a small change in frequency led to a large change in transmission. We accounted for the frequency uncertainty by including it in the transmission uncertainty using: 

\[ \Delta\tau' = \sqrt{ \Delta\tau^2 + (\Delta\nu \frac{d\tau}{d\nu})^2} \]

\textit{Line-Fit} numerically calculated the change in transmission per change in frequency, \( \frac{d\tau}{d\nu} \), from the spectral data. The uncertainty in the frequency measurements, \( \Delta\nu \), was an input constant estimated to be 0.2MHz (7\times10^{-6} \text{cm}^{-1}). This estimate is based on the standard deviation of infrared frequency measurements made with the visible lasers at a fixed frequency. This measurement therefore includes both measurement error and short-term drift of the lasers between measurements. Figure 5.3 shows a single line from a broader spectrum. The more closely spaced points in regions of rapidly changing transmission are evident, as are the increased error estimates due to the frequency uncertainty.
Fitting the line shape to the experimental absorption coefficient, $k(v)$, would require transforming the experimental error distribution (Duggan et al., 1993). To avoid this complication, Line-Fit performed the fitting in transmission space, meaning the least squares fit used the difference between the experimental transmission spectrum and the synthetic transmission spectrum calculated from the line shape parameters.

The synthetic transmission profile was constructed on a line by line basis with the total transmission profile determined by the product of the transmission profiles for individual lines. The absorption coefficient for each line, $k_n$, is a function of several global parameters that are common to all lines and many individual line shape parameters, $x_{ip}$.

$$
\tau(v) = B \prod_i \exp(-Lk_i(c, S_R, \gamma_R, v_{oo}, x_{i1}, x_{i2}, \ldots, x_{in})).
$$

The following table lists the global parameters.

<table>
<thead>
<tr>
<th>Global Parameter</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$, base line</td>
<td>ideally $B=1.0$</td>
</tr>
<tr>
<td>$L$, cell length</td>
<td>$L=107.05cm$</td>
</tr>
<tr>
<td>$S_R$, band strength factor</td>
<td>band strength is a scaling factor by which all the line strengths are scaled, ideally $S_R=1.0$</td>
</tr>
<tr>
<td>$\gamma_R$, Lorentz scaling factor</td>
<td>all the broadening parameters are scaled by this factor, ideally $\gamma_R=1.0$</td>
</tr>
<tr>
<td>$v_{oo}$, frequency offset</td>
<td>experimental relative frequency + $v_{oo}$ = real frequency</td>
</tr>
<tr>
<td>$c$, mixing ratio</td>
<td>has the same effect as the band strength above but also affects the broadening coefficients, ideally $c=1$</td>
</tr>
</tbody>
</table>

The baseline, $B$, has already been described above. The frequency offset, $v_{oo}$, adjusts the experimental, relative frequency axis such that it corresponds to the Hitran96 (Rothman et al., 1992a) frequency
Chapter 5: FIRST ORDER LINE MIXING - Spectral Fitting

axis. The band strength factor, $S_R$, was introduced so that the strength of the entire band could be fit rather than fitting for individual line strengths. Initially the length was introduced as an adjustable parameter to achieve the same effect. The Lorentz scaling factor, $\gamma_R$, was similarly defined so that all the lines could be simultaneously made wider or narrower. Both the strength factor and the Lorentz scaling factor allowed the fitting routine to adjust for small errors in the pressure without having to fit for the individual line parameters. The mixing ratio, $c$, was introduced when it was realised that some of the spectra had slight contamination with air. Not all the parameters are independent; for example the cell length and the band strength factor have identical effects on the line shape. The mixing ratio is also strongly correlated with the band strength factor and the broadening coefficient factor. The reasons for the former are that we are actually fitting the optical thickness which is proportional to the product, $cL S_R$. The correlation between the mixing ratio and the broadening coefficient factor arises because the broadening parameter is defined to be $\gamma = \gamma_R \cdot (c \gamma_{self} + (1-c) \gamma_{foreign})$.

For each spectral branch, a separate data file contained all the spectral information of the lines to be included in the synthetic spectrum. Lines from the $P$, $Q$, and $R$-branches of $^{12}\text{C}^{16}\text{O}_2$ were included, as were lines from several other overlapping bands. All CO$_2$ lines between 2076.8 cm$^{-1}$ and 2078.7 cm$^{-1}$ with Hitran96 (Rothman et al., 1992b) strengths of greater than $5 \times 10^{-26}$ cm$^{-1}/$(mol·cm$^{-2}$) were included, as were other strong lines in the broader range 2075 cm$^{-1}$ to 2080 cm$^{-1}$. In addition, the $P(16)$ line of CO fell within the region measured and so was included in the analysis. By measuring the strength of the CO $R(6)$ line at 2169 cm$^{-1}$ the concentration of CO in our cylinder of CO$_2$ was determined to be 0.6 ppm. Although Line-Fit used all the above-mentioned lines in the synthetic spectrum, it was restricted to fit only lines with their line centres within the range of the spectral data. This prevented lines from being fit where only one wing of the line was evident in the spectrum.

The Line-Fit user can select one of several line shape models to fit to the spectral data. The various models and associated parameters are listed in table 5.2. In each case, only selected free parameters were fit.

The fitting algorithm was the well known Levenberg Marquardt algorithm. We used a version adapted from “Numerical Recipes in C” (Press et al., 1992). The Levenberg Marquardt algorithm is a robust least squares fitting program, capable of optimising a large number of free parameters.
quickly. The algorithm calculates the best fit parameters and their associated error estimates. Although robust, a local minimum can still fool the Levenberg Marquardt algorithm and prevent it from finding the best fit. A simple test to identify a local minimum is to look for convergence to a different minimum when fitting the same data more than once using different initial parameters. In fact there is no test that will prove a solution to be global and the possible existence of a local minimum must always be considered when examining the results. It was found that optimum convergence required a good initial guess and was particularly sensitive to the initial frequency offset, $v_\infty$. The parameter $v_\infty$ was manually adjusted, by eye, within the Line-Fit program. The difference between the spectral data and the initial guess was displayed on screen while the frequency offset parameter was adjusted. The frequency was adjusted to minimise asymmetric structures which result when the synthetic spectra are not correctly aligned with the experimental spectra.

<table>
<thead>
<tr>
<th>Model Type</th>
<th>Line Shape Composition</th>
<th>Free Parameters</th>
<th>Fixed Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lorentz</td>
<td>sum of a symmetric and an asymmetric Lorentz profile</td>
<td>$\gamma$, $v_0$, $P$, $Q$</td>
<td></td>
</tr>
<tr>
<td>hard collision</td>
<td>sum of a symmetric and an asymmetric hard collision profile</td>
<td>$\gamma$, $v_0$, $P$, $Q$, $z$</td>
<td></td>
</tr>
<tr>
<td>speed-dependent hard collision, A</td>
<td>sum of two symmetric and two asymmetric hard collision profiles</td>
<td>$\gamma$, $v_0$, $P$, $Q$, $z$</td>
<td>$r_{\tau_1}=\gamma_1/\gamma$, $r_{\tau_2}=\gamma_2/\gamma$, $r_{p_1}=p_1/p=q_1/q$, $r_{p_2}=p_2/p=q_2/q=1-r_{p_1}$</td>
</tr>
<tr>
<td>speed-dependent hard collision, B</td>
<td>sum of two symmetric and one asymmetric hard collision profiles</td>
<td>$\gamma$, $v_0$, $P$, $Q$, $z$</td>
<td>$r_{\tau_1}=\gamma_1/\gamma$, $r_{\tau_2}=\gamma_2/\gamma$, $r_{p_1}=p_1/p$, $r_{p_2}=p_2/p=1-r_{p_1}$</td>
</tr>
</tbody>
</table>
Chapter 5: FIRST ORDER LINE MIXING - Spectral Fitting

The most basic and computationally fastest line shape model was the Lorentz line shape with asymmetry (mixing), equation 2.15, but the hard collision model of equation 5.12 was used more extensively because it included Doppler broadening and Dicke narrowing. The hard collision model requires the calculation of the complex probability integral (equation 5.3) for which we used the plasma dispersion function, \( Z(\zeta = x + iy) \), used by Duggan (1995). The plasma dispersion function is related to the complex probability integral through \( \nu(\zeta) = Z(\zeta)/i\pi^{1/2} \) (Fried and Conte, 1961). This algorithm was compared to the more commonly used algorithm for calculating the complex probability integral of Humlíček (1979) and the differences were found to be negligible.

The Levenberg Marquart algorithm uses derivatives of the line shapes with respect to each of the free parameters in its calculations. For each model, the derivatives were expressed analytically, although for the hard collision model the derivatives are algebraically complex. In calculating the derivatives for the hard collision model we used the identity, \( Z'(\zeta) = -2(1 + \zeta Z) \) (Fried and Conte, 1961).

To prevent non-physical solutions, all parameters were constrained to remain within a defined range. This was only observed to be of importance for the Dicke narrowing parameter, \( z \), which was constrained to remain positive and less than 1000. This enhanced the numerical stability of the algorithm and prevented singularities.

The Levenberg Marquardt algorithm assumed the model to be correct and that the error in the fits arose solely from noise in the data. At times it will be clear that this was a bad assumption. When the residual spectrum (spectral data - calculated spectra) lies outside the estimated error based on the noise in the data, one must consider both the limitations of the model and the accuracy of the noise estimates. The Levenberg Marquardt algorithm uses \( \chi^2 \) as a measure of the size of the residual in terms of the uncertainty in the data\(^{16} \). If the noise estimates, \( \sigma \), are correct and the model fits the

\[^{16}\text{The standard definition of } \chi^2 \text{ is:}\]

\[ \chi^2 = \sum_{i=1}^{n} \left( \frac{\text{data}_i - \text{fit}_i}{\sigma_i} \right)^2 \]

where \( \sigma \) is the one standard deviation noise estimate in the data point.
spectrum within the noise estimates, then $\chi^2$ should equal the total number of degrees of freedom which is the total number of points in the spectrum, $n$, less the number of fitting parameters, $n_f$. Since each spectrum consisted of several hundred points we approximated the total number of degrees of freedom by the total number of points, $n = n - n_f$. The error estimate for each fit parameter is the change in that parameter from its optimum value that will increase $\chi^2$ by 1. If the model cannot fit the data within the noise, then $\chi^2$ will be larger than $n$, and the calculated error estimate will be too small. For all our fits, $\chi^2$ was indeed larger than $n$ and to correct for this, Line-Fit multiplied the error estimate calculated for each fit parameter by $(\chi^2/n)^{0.5}$. This was equivalent to increasing the noise estimates such that the best fit fell within the noise. This factor ranged from 3 for high pressure fits and up to 10 for low pressure fits.

Typical noise estimates, $\sigma$, predict a signal-to-noise ratio up to 15 000:1 and clearly we have not achieved this level of performance yet. These noise estimates are based on the standard distribution of samples taken at one frequency and therefore only measure the random noise at that point in the spectrum. This noise estimate does not include sources of error that change from point to point such as we see in a baseline spectrum. We have concluded that these point to point variations are significant particularly for low pressure spectra with smaller absorption. It is these sources of error that are being included by the factor $(\chi^2/n)^{0.5}$.

What remains significant about the original noise estimates, $\sigma$, is their relative size. In general the raw error estimates are found to be fairly constant across a spectrum but are then adjusted to be larger on the steep slopes of the absorption features. Hence points in flatter regions are weighted more heavily in the fits. Since the point spacing is higher in the rapidly changing regions, the various regions of the spectrum are roughly equally weighted in the fit.

The program was very flexible which encouraged experimentation with different fitting methods. For each spectrum, any combination of line shape parameters and global parameters could be selected to be fit or not fit. It was possible to fit different parameters to different lines or even to use different line shape models for different lines.
5.3 SPECTRAL RESULTS

5.3.1 Low Pressure Spectra

Doppler broadening is significant at low pressures. The relative importance of translational and collisional effects at 301K and 1.4kPa can be estimated from the Doppler half-width, 58MHz ($1.9 \times 10^3 \text{ cm}^{-1}$), and typical Lorentz half-width, 42MHz ($1.4 \times 10^3 \text{ cm}^{-1}$). The line shape at low pressures is very close to the Voigt line shape since both Dicke narrowing and line mixing effects are relatively small.

Since the overall widths of these lines are quite small, the low pressure spectra have well resolved absorption features. This makes low pressure spectra ideal for measuring the relative frequencies of the absorption lines. We ignored any pressure shifting since typical linear pressure shift coefficients are on the order of 50MHz/atm ($-2 \times 10^3 \text{ cm}^{-1}$/atm) (Sinclair et al., 1997) which results in only a 0.7MHz ($2 \times 10^5 \text{ cm}^{-1}$) shift at 1.4kPa. This assumption will be justified later when we present the linear pressure shift coefficient we measured. A low pressure fit for line frequencies and asymmetries showed that these two parameters were highly correlated. At 1kPa the correlation coefficient ranged from (-0.6) for most lines to (-0.8) for the $Q(2)$ line. In addition, these lines are predominantly Doppler broadened, and thus it was difficult to extract reliable line mixing measurements from the spectra. For the low pressure spectra, we therefore decided to fix the line mixing coefficients, $Y_n$, to the first order quantities derived by Strow et al. (1994) and fit the broadening, narrowing, and line strength parameters for each line.

The results of such fits clearly showed systematic differences existed between the measured relative frequencies and those listed in Hitran96 (Rothman et al., 1992a). Figure 5.4 shows the averaged results from 16 low pressure spectra. The slope of the line can be easily be explained by a single calibration factor. Since the frequency differences in Hitran96 are considered very precise, we chose to adjust our frequency scale in order to bring our measurements in line with Hitran96 values. In doing this we essentially re-calibrated our Fabry-Perot against Hitran96. The original Fabry-Perot free spectral range (FSR), based on a decade-old travelling microscope measurement of the Fabry-Perot length, was 301.69(12)MHz ($1.00633(40) \times 10^2 \text{ cm}^{-1}$). The slope of the best fit line in figure 5.4
goes to zero if the FSR is corrected to 301.932(1)MHz \( \times 10^{2}\text{cm}^{-1} \). All further analysis used a corrected experimental frequency axis, \textit{i.e.} the experimental frequencies were divided by a correction factor, \( 0.999198 = \frac{301.69\text{MHz}}{301.932\text{MHz}} \).

![Graph](Image)

Figure 5.4. Calibration of the Fabry-Perot free spectral range against the Hitran96 data base.

Figure 5.5 shows a typical low pressure absorption spectrum and the small residual (data-fit). In the enlarged view of the residual we see that the noise is largest on the steep part of the curves, suggesting that it arose mainly from an uncertainty in the infrared frequency.
5.3.2 Medium Pressures

In the medium pressure range the line shape becomes increasingly collision broadened. With increasing pressure, collisional effects broaden each line and adjacent lines overlap further, particularly the Q(2) and Q(4) lines. Dicke narrowing increases with increasing pressure which leads to a reduction in the width of the translational component of the line shape. It is in this pressure region that Dicke narrowing effects are most apparent. Line mixing also becomes an important line shape feature with the dominant observable features being well explained by the Rosenkranz first order approximation.

The medium pressure region offers the opportunity to observe line mixing in a pressure regime where the individual lines are still resolved. From the medium pressure data, using the Rosenkranz approximation.
approximation we extracted the line broadening coefficients, the narrowing parameters, the first order line mixing coefficients, the band's linear pressure shift coefficient, and the band strength.

Pressure can induce frequency shifts of the active molecule to either higher or lower frequencies. At low pressures the shift is proportional to pressure and is characterised by a linear pressure shift coefficient, \( \delta \), which is in general a function of the rotational level (May et al., 1964; Green, 1979). If the largest component of the linear pressure shifting is the vibrational phase shift then, to first order, the entire \( Q \)-branch shifts together as a whole. Evidence does suggest that the shifts are relatively \( J \) independent or at least the differences are very small at these pressures. In fact, calculations by Thibault et al. (1992) predict zero linear pressure shifts for \( Q \)-branches. Measurements reported by Strow and Pine (1988) found the fitted pressure shifts for an \( N_2O \) \( Q \)-branch to be \( J \) independent and small, \(-2.6 \times 10^{-3}\) cm\(^{-1}\)/atm. If we can consider the line shifts of \( P \) and \( R \) lines as worst case estimates of rotational dependence for the \( Q \)-branch, measurements by Sinclair et al. (1997) show little variation for CO in He. Hence, fixing the relative frequency spacings of the lines at the Hitran96 values should introduce little error. This assumption prevents the fitted line positions from coupling to fitted line mixing parameters with which they are highly correlated. The assumption of \( J \) independent shifting is also made by others (Bonamy et al., 1988; Lavorel et al., 1990a; 1990b; Margottin-Maclou et al., 1992).

The relative line strengths were also fixed and only the vibrational band intensity was allowed to float in the fitting routine. Each of these assumptions removed a degree of freedom for each line to be fit, which for a spectrum containing 14 lines, reduced the number of fit parameters by 28. The parameters allowed to float in the fitting routine were the half-widths \( \gamma_p \), the narrowing parameters \( \gamma_r \), and the mixing parameters \( \gamma_n \), plus the frequency offset, band strength factor and baseline offset. Thus there was a total of 45 parameters for a 14 line spectrum.
Chapter 5: FIRST ORDER LINE MIXING - Medium Pressure

Table 5.3. A comparison of measurements of the $v_1 + v_2$ band strength.

<table>
<thead>
<tr>
<th>Authors</th>
<th>$10^{21} \times$ Band Intensity $\text{ cm}^{-1}$/(molecule$\cdot$cm$^2$)</th>
<th>Temperature</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>4.03(2)</td>
<td>296</td>
<td></td>
</tr>
<tr>
<td>Rinsland et al. (1986)</td>
<td>4.155(11)</td>
<td>296</td>
<td></td>
</tr>
<tr>
<td>Gentry and Strow (1987)</td>
<td>3.96(3)</td>
<td>296</td>
<td></td>
</tr>
<tr>
<td>Arcas et al. (1982)</td>
<td>3.95(3)</td>
<td>296</td>
<td></td>
</tr>
</tbody>
</table>

We first consider the properties of the band. The $(v_1 + v_2)$ band intensity used by Hitran96 is the value of Rinsland et al. (1986) of $4.155(11) \times 10^{21} \text{ cm}^{-1}$/(molecule$\cdot$cm$^2$) at 296K which is then adjusted to the temperature required. Because the $v_2$ vibration is of relatively low energy (667 cm$^{-1}$), the population of the ground vibrational level is affected by thermal excitation to the first vibrational level. The band strength of CO$_2$ is therefore more dependent on temperature than other molecules where the first vibrational energy level is higher. Hitran96 corrects for the change in band strength using a polynomial representation of the partition function (Gamache et al., 1990). In addition, Hitran96 also corrects for vibration-rotation interaction using Herman-Wallis coefficients. The band intensity determined from the fits of medium pressure spectra was 0.970(5) of the Hitran96 vibrational band intensity given at 301K. Our measured band intensity therefore corresponds to $4.03(2) \times 10^{21} \text{ cm}^{-1}$/(molecule$\cdot$cm$^2$) at 296K, where our error estimate was obtained from the run-to-run variation. The dominant source of error in this result arose from the baseline uncertainty since the uncertainty in the pressure and cell length were negligible.

Table 5.3 compares our vibrational band intensity with the measurements of several other groups. The measurement does not agree within the stated error limits with the Fourier transform measurement of Rinsland et al. (1986) whose value is the basis for Hitran96 value. Arcas et al. (1982)
also made measurements of this band using a grating spectrometer. Rinsland et al. compared their measurements with those of Arcas et al. and concluded that the agreement was quite good, despite the small errors given to both works. The diode laser measurements of Gentry and Strow agree within error with those of Arcas et al.. Both Gentry and Strow, and Arcas et al. used the method of equivalent widths (Jansson and Korb, 1968) to determine the band strength as opposed to the direct curve fitting technique used by us and Rinsland et al.. Given the higher frequency resolution of the difference frequency system and better baseline determination of than the other experimental techniques we believe our strength measurement to be a more accurate value for this band.

The shifting of the band was within the measurement capability of our system. For each pressure at or below 11kPa we determined the shift with respect to a 0.7kPa or 1.3kPa spectrum and then linearly extrapolated the results to determine the shift from the frequency for the free streaming molecule (0kPa). The results for each pressure are plotted in figure 5.6. The calculated linear pressure

![Figure 5.6. Shifting measurements from medium pressure spectra. The regression was forced through the origin to give a shift of $\delta_o = -46(2)$ MHz/atm.](image)

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Table 5.4. Comparison of pressure shift coefficients for $Q$-branches.

<table>
<thead>
<tr>
<th>Author</th>
<th>Shift</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Our experiment</td>
<td>$-1.54(7) \times 10^{-3}\text{cm}^{-1}\text{atm}$</td>
<td>pure CO$_2$, $v_1+v_2$</td>
</tr>
<tr>
<td>Lavorel et al., (1990a)</td>
<td>$-11.3(6) \times 10^{-3}\text{cm}^{-1}\text{atm}$</td>
<td>pure CO$_2$, $2v_2$</td>
</tr>
<tr>
<td>Lavorel et al., (1990b)</td>
<td>$-8.1(3) \times 10^{-3}\text{cm}^{-1}\text{atm}$</td>
<td>pure CO$_2$, $v_1$</td>
</tr>
<tr>
<td>Roland and Steele, (1981)</td>
<td>$-10.2 \times 10^{-3}\text{cm}^{-1}\text{atm}$</td>
<td>pure CO$_2$, $v_1$</td>
</tr>
<tr>
<td>Margottin-Maclou et al., (1992)</td>
<td>$-7.1 \times 10^{-3}\text{cm}^{-1}\text{atm}$</td>
<td>pure N$_2$O</td>
</tr>
<tr>
<td>Strow and Pine, (1988)</td>
<td>$-2.6 \times 10^{-3}\text{cm}^{-1}\text{atm}$</td>
<td>pure N$_2$O</td>
</tr>
</tbody>
</table>

The shift of the branch was determined to be $\delta_o = -46.4(20)\text{ MHz/atm}$ ($1.54(7) \times 10^{-3}\text{cm}^{-1}\text{atm}$). The shift and error were determined by a linear regression that was forced through the origin. The fit is strongly affected by the lone point at 10.6kPa but refitting the results without this point only reduces the shift to $43.3(2)\text{ MHz/atm}$. This result can be compared with other $Q$-branch shift measurements listed in table 5.4. These measurements are all for different bands and in the case of the last two are for different gases. We should not therefore expect the results to agree within error. However, note that all the results are negative and of the same order of magnitude and clearly not zero as claimed by the theory of Thibault et al. (1992b). Most of these measurements were performed on spectra where the branch had largely collapsed to a single feature. Measurements under these conditions are sensitive to the methods by which line mixing is incorporated into the fit. Only our work and that of Strow and Pine (1988) was performed at low pressures where individual lines can be resolved.

We now turn to the details of fitting the band. As an example of a fit, figure 5.7 shows a 6.6kPa spectrum and the residual to the fit. The lines are relatively narrow and, with the exception of the $Q(2)$ and $Q(4)$ lines, are individually resolved. Because the line overlap is small, the line mixing is weak, but nevertheless measurable. As discussed for low pressures in connection with figure 5.5, the residual in figure 5.7 is dominated by the errors in the frequency measurements. No discernable structure is evident in the residual, indicating the ability of the model to fit the spectrum.
Figure 5.7. Fit to a 6.6kPa spectrum, with residual.
Figure 5.9 shows, as a sample, the pressure-broadened half widths (HWHM) versus pressure for lines $Q(2)$, $Q(10)$ and $Q(22)$. The error estimates (determined from the spectral fits) increase for the high pressure spectra, particularly for the $Q(2)$ line, due to the increasing overlap of the adjacent lines. The linearity of the relationship between width and pressure is good. For each line between $Q(2)$ and $Q(32)$, the half widths measured at each pressure were scaled to one atmosphere and averaged over all spectra below 11 kPa to obtain the broadening coefficients. Although the collisional widths are small at these pressures, the variation in broadening coefficients determined from spectrum

![Figure 5.8. Measured line widths versus pressure.](image)

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Figure 5.9. A comparison of our line width measurements corrected to 296K with the results of two other authors.

to spectrum was less than 0.5%. Figure 5.9 shows the agreement between the broadening parameters we determined, those of Gentry and Strow (1987), and those reported by Hitran96 (Rothman et al., 1992b). The most significant difference occurs for $Q(2)$. The broadening parameters reported by Hitran96 are generic for all branches of CO$_2$ because it is assumed that there is little sensitivity of the half-widths to vibrational mode (Mandin et al., 1994). Table 5.5 contains our pressure broadening coefficients at 301K along with the results of other groups. The results of Johns

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### Table 5.5 Broadening coefficient measurements.

<table>
<thead>
<tr>
<th>Band</th>
<th>$\gamma_0$</th>
<th>Gentry and Straw</th>
<th>Dana et al.</th>
<th>Johns</th>
<th>Hitran96</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm$^{-1}$/atm</td>
<td>(cm$^{-1}$/atm)</td>
<td>(cm$^{-1}$/atm)</td>
<td>(cm$^{-1}$/atm)</td>
<td>(cm$^{-1}$/atm)</td>
</tr>
<tr>
<td>$m \backslash$ Band</td>
<td>$v_1+v_2$</td>
<td>$v_1+v_2$</td>
<td>00011-10001</td>
<td>01111-01101</td>
<td>All bands</td>
</tr>
<tr>
<td>2</td>
<td>0.1203(17)</td>
<td>0.1343</td>
<td>0.1190</td>
<td>0.1214</td>
<td>0.1228</td>
</tr>
<tr>
<td>4</td>
<td>0.1165(5)</td>
<td>0.1175</td>
<td>0.1162</td>
<td>0.1173</td>
<td>0.1190</td>
</tr>
<tr>
<td>6</td>
<td>0.1129(5)</td>
<td>0.1137</td>
<td>0.1108</td>
<td>0.1124*</td>
<td>0.1141</td>
</tr>
<tr>
<td>8</td>
<td>0.1094(3)</td>
<td>0.1098</td>
<td>0.1074</td>
<td>0.1115</td>
<td>0.1116</td>
</tr>
<tr>
<td>10</td>
<td>0.1063(4)</td>
<td>0.1070</td>
<td>0.1066</td>
<td>0.1074</td>
<td>0.1091</td>
</tr>
<tr>
<td>12</td>
<td>0.1037(3)</td>
<td>0.1072</td>
<td>0.1053</td>
<td>0.1042</td>
<td>0.1067</td>
</tr>
<tr>
<td>14</td>
<td>0.1018(3)</td>
<td></td>
<td>0.1025</td>
<td>0.1038</td>
<td>0.1043</td>
</tr>
<tr>
<td>16</td>
<td>0.0996(3)</td>
<td></td>
<td>0.1015</td>
<td>0.1009</td>
<td>0.1020</td>
</tr>
<tr>
<td>18</td>
<td>0.0979(3)</td>
<td></td>
<td>0.0988</td>
<td>0.0990</td>
<td>0.0998</td>
</tr>
<tr>
<td>20</td>
<td>0.0961(6)</td>
<td>0.0974*</td>
<td>0.0994</td>
<td></td>
<td>0.0977</td>
</tr>
<tr>
<td>22</td>
<td>0.0945(4)</td>
<td>0.0956</td>
<td>0.0973*</td>
<td></td>
<td>0.0956</td>
</tr>
<tr>
<td>24</td>
<td>0.0925(5)</td>
<td>0.0937</td>
<td>0.0959</td>
<td></td>
<td>0.0935</td>
</tr>
<tr>
<td>26</td>
<td>0.0906(5)</td>
<td>0.0902*</td>
<td>0.0917</td>
<td></td>
<td>0.0916</td>
</tr>
<tr>
<td>28</td>
<td>0.0886(7)</td>
<td>0.0869</td>
<td>0.0893*</td>
<td></td>
<td>0.0897</td>
</tr>
<tr>
<td>30</td>
<td>0.0867(6)</td>
<td>0.0885</td>
<td>0.0882</td>
<td></td>
<td>0.0878</td>
</tr>
<tr>
<td>32</td>
<td>0.0848(5)</td>
<td>0.0856</td>
<td>0.0882</td>
<td></td>
<td>0.0860</td>
</tr>
</tbody>
</table>

a) For the $R$-branch $m=j+1$, $P$-branch $m=j$, and $Q$-branch $m=j$. For comparison the $P$- and $R$-branch measurements are presented as $\gamma_p=[\gamma_{m+1}+\gamma_{m+1}]/2$. An * indicates that either $\gamma_m$ or $\gamma_{m+1}$ was not available.
b) Our $Q$-branch measurements were made at 301K.
c) Gentry and Straw’s (1987) measurements are from a single 100 Torr fit of the same $v_1+v_2$ $Q$-branch at 296K.
d) The results of Dana et al. (1992) are from $P$- and $R$-branch measurements in the laser band region at 294K.
e) The results of Johns (1987) are from $P$- and $R$-branch measurements made in a hot band near 4.3 $\mu$m at 300K.
f) Hitran96 (Rothman et al., 1992b) uses a collection of results and assumes the widths to be band and branch independent.
Figure 5.10. The measured narrowing coefficient versus pressure for the
(Q(6) and (A): Q(16) lines. (---) is the narrowing coefficient
calculated from the diffusion constant \( D=0.117 \text{ (cm}^2\text{sec}^{-1}) \)
(1987) and Dana et al. (1992) are for different bands but are in reasonable agreement with our results,
indicating that the broadening in \( \text{CO}_2 \) is reasonably band insensitive.

Figure 5.7 might suggest that the model fits the spectra well at medium pressures. However,
the behaviour of the narrowing parameters derived from the model is unphysical. As discussed earlier
the narrowing parameter is inversely related to the diffusion constant and hence should scale linearly
with pressure. Figure 5.10 shows that the relationship between the measured narrowing parameter
and pressure is strongly non-linear, although at pressures less than 1.3kPa the narrowing parameter
does agree with that predicted by the mass diffusion constant. These results are consistent with those
of Duggan et al. (1993) in \( \text{CO}_2 \). Since we used the hard collision model which fails to account for
speed dependence, the derived Dicke narrowing parameter tends to compensate for the effects caused
by speed dependence (Duggan et al., 1995; Berman, 1972). Some \( J \) dependence of the narrowing
parameters was found at pressures above 2.5kPa with the strongest non-linear dependence found for
strongest lines. The J dependence will not be investigated further in this thesis but is thought to be further evidence that the line shape model we use is not physically correct.

It was found that at pressures higher than 11kPa the narrowing parameter could no longer compensate for the speed-dependent effects. This led to the requirement for a line shape model that accounted for speed-dependent effects, and a different analysis method for the higher pressure spectra which is discussed in the next chapter.

5.3.3 First Order Line Mixing Results

The mixing parameters were measured over the range of medium pressures for each line. As a sample, figure 5.11 shows mixing parameters, $Y_j$, for the $Q(2)$, $Q(4)$ and $Q(16)$ lines as a function of pressure. For $Q(2)$ and $Q(4)$ the linearity of the mixing parameter with pressure is very apparent. Using results like those shown in figure 5.11, the mixing coefficients in table 5.6 were determined for each line by a linear regression, forcing the fit to pass through the origin. Figure 5.12 shows a plot of the mixing coefficients, $Y_j$, as a function of J. As expected, the line mixing coefficient varies considerably throughout the band, both in magnitude and sign. That the line mixing coefficient is positive for low J and negative for high J is a signature that the band is collapsing. Also shown are the line mixing coefficients calculated from the relaxation matrix calculated using the Exponential Power Gap (EPG) law which will be discussed in the next section.

The relaxation matrix results are in reasonable agreement with the measured values. Both figure 5.12 and table 5.6 serve to show that the general behaviour of the measured mixing coefficients is similar to that predicted by the scaling law calculation. In the measured data, the mixing is greatest for lines $Q(2)$ and $Q(4)$ and changes sign near $Q(10)$. The J dependence is somewhat different for the EPG approach which predicts a sign change nearer to $Q(8)$ and a maximum negative mixing around $Q(18)$.

We emphasis that these line mixing results are direct measurements of line mixing and have only been constrained in that the relative line strengths have been assumed constant and the line shifts have been assumed equal. Both these assumptions are consistent with the Rosenkranz first order approximation. The Rosenkranz approximation also requires that the mixing parameter vary linearly
Figure 5.11. Measured mixing parameters versus pressure. Note the different scales above and below the zero line, with pressure as has been observed in the data.
Figure 5.12. Measured first order line mixing coefficients versus J, shown with error bars. Solid line shows mixing coefficients determined from the EPG law calculation with $\beta=0.56$. 

Chapter 5: FIRST ORDER LINE MIXING - Medium Pressure
Table 5.6. Comparison of measured first order mixing coefficients, those predicted by our relaxation matrix, and those given by Strow et al. (1994).

<table>
<thead>
<tr>
<th>J</th>
<th>$Y_o$ at 301K Experimental$^a$ (atm$^{-1}$)</th>
<th>$Y_o$ at 301K Calculated$^b$ (1/atm$^{-1}$) $\beta=0.50$</th>
<th>$Y_o$ at 301K Calculated$^b$ (1/atm$^{-1}$) $\beta=0.56$</th>
<th>$Y_o$ at 301K Calculated by Strow$^c$ (atm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.82(2)</td>
<td>2.50</td>
<td>2.807</td>
<td>2.79</td>
</tr>
<tr>
<td>4</td>
<td>0.58(1)</td>
<td>0.55</td>
<td>0.608</td>
<td>0.54</td>
</tr>
<tr>
<td>6</td>
<td>0.19(1)</td>
<td>0.16</td>
<td>0.170</td>
<td>0.13</td>
</tr>
<tr>
<td>8</td>
<td>0.06(1)</td>
<td>0.013</td>
<td>0.013</td>
<td>0.000</td>
</tr>
<tr>
<td>10</td>
<td>0.005(10)</td>
<td>-0.050</td>
<td>-0.056</td>
<td>-0.057</td>
</tr>
<tr>
<td>12</td>
<td>-0.032(9)</td>
<td>-0.080</td>
<td>-0.089</td>
<td>-0.083</td>
</tr>
<tr>
<td>14</td>
<td>-0.056(8)</td>
<td>-0.095</td>
<td>-0.104</td>
<td>-0.096</td>
</tr>
<tr>
<td>16</td>
<td>-0.075(7)</td>
<td>-0.101</td>
<td>-0.111</td>
<td>-0.101</td>
</tr>
<tr>
<td>18</td>
<td>-0.080(6)</td>
<td>-0.102</td>
<td>-0.113</td>
<td>-0.103</td>
</tr>
<tr>
<td>20</td>
<td>-0.092(5)</td>
<td>-0.101</td>
<td>-0.112</td>
<td>-0.102</td>
</tr>
<tr>
<td>22</td>
<td>-0.109(4)</td>
<td>-0.098</td>
<td>-0.109</td>
<td>-0.100</td>
</tr>
<tr>
<td>24</td>
<td>-0.111(5)</td>
<td>-0.094</td>
<td>-0.105</td>
<td>-0.097</td>
</tr>
<tr>
<td>26</td>
<td>-0.120(6)</td>
<td>-0.090</td>
<td>-0.101</td>
<td>-0.094</td>
</tr>
<tr>
<td>28</td>
<td>-0.127(14)</td>
<td>-0.085</td>
<td>-0.096</td>
<td>-0.091</td>
</tr>
<tr>
<td>30</td>
<td>-0.122(6)</td>
<td>-0.081</td>
<td>-0.091</td>
<td>-0.087</td>
</tr>
</tbody>
</table>

a) Our experimental results of line mixing.  
b) Line mixing calculated using the relaxation matrix estimated from an EPG law and our broadening parameters.  
c) Line mixing calculated by Strow et al. (1994) with $\beta=0.54$.  

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5.3.4 Exponential Power Gap (EPG) Law Calculation

The procedure for calculating the relaxation matrix from the broadening coefficients was described in the theory chapter. The EPG law used to relate the collision rate from state $k$ to $j$ is given by (Gentry and Strow, 1987)

$$\kappa_{jk} = a \left( \frac{|\Delta E_{jk}|}{k_b T} \right)^{-b} \exp \left( -c \frac{|\Delta E_{jk}|}{k_b T} \right), \quad (5.17)$$

where $\Delta E_{jk}$ is the energy difference between the lower energy states of two transitions, and $k_b T$ has its usual meaning. The parameters to be optimised are $a$, $b$, and $c$. With the EPG law, detailed balance, and the modified sum law, the diagonal elements of the relaxation matrix, $W_{jj}$, can be determined for any set of constants $a$, $b$, and $c$. The constants are determined such that the calculated $W_{jj}$ match the measured $\gamma_j$ in a least squares sense. This technique was applied to the band we measured using our measurements of line widths.

We wrote a C++ program called Scaling to perform the gap law calculation. A data file supplied the necessary spectroscopic information: rotational quantum numbers, line frequencies, line strengths, broadening coefficients, lower energy state levels, and weighting factors. For rotational states belonging to forbidden transitions only the lower energy level was required. Ideally this calculation would include all lines in the band but this was unfeasible. We ran the program with broadening coefficients for lines $Q(2)$ to $Q(58)$. For reasons that will be discussed later, each broadening coefficient had an associated weighting factor. These were just relative factors used to emphasise the importance of fitting some broadening coefficients over others.

Line mixing between overlapping lines belonging to different branches is possible (Green, 1989; Hartmann and Boulet, 1991; Hartmann and L’Haridon, 1995) so long as collisions can couple both the initial and final states. In the branch we study, such an example might exist between the $R(0)$ and $Q(26)$ lines which are located at 2077.636699cm$^{-1}$ and 2077.644661cm$^{-1}$ respectively. We have assumed the interaction to be negligible since the $J=0$ (or $J=1$) and $J=26$ rotational levels are well separated (~273cm$^{-1}$).

Evidence suggests that CO$_2$ lines are at least 95% broadened by inelastic collisions (Lavorel et al., 1990a; 1990b) and so we will assume that rotationally inelastic collisions contribute 100% of
the line width and hence $\gamma_d = 0$. The broadening coefficients for lines $Q(2)$ to $Q(32)$ were our experimental values at 301K taken from table 5.5. For lines $Q(34)$ to $Q(58)$ the broadening coefficients were taken from Hitran96, also at 301K. The lower state energy levels, line frequencies, and line strengths were taken from Hitran96. For the odd levels, only the lower state energy levels were required, and these were interpolated from the even levels. The band strength was not adjusted to our measured value but this only changed the band shape by a multiplicative factor which could be corrected by the band strength factor, $S_R$.

The output from Scaling included the relaxation matrix, as well as the first and second order line mixing coefficients. Rosenkranz's first order equation, 2.16, was used to calculate the first order mixing coefficients while Smith's second order equations, 2.19 and 2.20, were used to calculate the quadratic pressure shift coefficients and the quadratic strength coefficients.

An important input parameter, $\beta$, was described in the theory chapter as reflecting the preference for even-even collisions over even-odd collisions. This parameter cannot be determined from the information given to Scaling. Strow et al. (1994) optimised this parameter based on comparisons between calculated and experimental spectra. Alternatively we select $\beta$ on to give agreement between calculated and measured line mixing coefficients for the $Q(2)$. 

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Figure 5.13. The diagonal elements of the relaxation matrix minus the broadening coefficients used in the GAP law calculation.

The initial run of Scaling had equal weighting for all line widths. Figure 5.13 shows the difference between the diagonal components of the calculated relaxation matrix and the line widths used in the calculation. It is not unexpected that the artificial cutoff at $Q(58)$ created problems. Collisional transitions between rotational state $J=58$ and higher states must contribute a significant fraction of the $Q(58)$ line width. Thus, the abrupt cutoff requires that the collision rates with rotational levels 54 and 56 be increased. But in distorting the relaxation matrix to fit the broadening coefficients of the high $J$ lines, the broadening coefficients of the lower $J$ lines are affected. Because the high $J$ lines are much smaller in strength and farther away from the region of spectral interest, it is not as important that the line widths for the high $J$ lines are as well modelled as the low $J$ lines by the relaxation matrix. A second run used relative weightings of 0.1 for all lines $Q(52)$ and higher. Figure 5.13 shows that the fit to the stronger, more important lines is improved.
Figure 5.14. Predicted line mixing. The amount of mixing predicted by the relaxation matrix is shown to increase with $\beta$. The two horizontal lines show the measured line mixing of the $Q(2)$ and $Q(4)$ lines.

To evaluate the impact of the $\beta$ parameter, Scaling was run with values of $\beta=0.5, 0.54, 0.55, 0.56, \text{and } 0.60$, remembering from its definition that as $\beta$ increases, even-even collisions are increasingly favoured over even-odd collisions. The largest difference between the runs was in the value of the line mixing coefficient for $Q(2)$. When Strow et al. (1994) fit spectra for different values of $\beta$, they were effectively adjusting the size of the line mixing effects which are dominated by the $Q(2)$ mixing term, at these pressures. Figure 5.14 shows a plot of first order mixing versus $\beta$ for both the $Q(2)$ and $Q(4)$ lines. The results in figure 5.14 show that an increase in $\beta$ leads to a roughly linear increase in first order line mixing. The first order mixing coefficients for the higher $J$ lines show a similar increase with $\beta$, but the absolute magnitude of the change is much less. The value $\beta=0.56$ gives best agreement with this first order mixing coefficient of $Q(2)$, $P_{2}^{\alpha}=2.82$. Strow et al. (1994) found a best fit to spectral data with $\beta=0.54$. It must be remembered that they used somewhat different values for the broadening coefficients in the relaxation matrix calculation.
Table 5.7. Quadratic coefficients calculated from the relaxation matrix with $\beta=0.56$.

<table>
<thead>
<tr>
<th>Line</th>
<th>$10^3 \times$ Quadratic Pressure Shift Coefficient (cm$^4$/atm$^2$)</th>
<th>Quadratic Strength Coefficient (atm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>8.755</td>
<td>-4.3600</td>
</tr>
<tr>
<td>4</td>
<td>-1.522</td>
<td>1.1498</td>
</tr>
<tr>
<td>6</td>
<td>-1.583</td>
<td>0.4812</td>
</tr>
<tr>
<td>8</td>
<td>-1.220</td>
<td>0.2117</td>
</tr>
<tr>
<td>10</td>
<td>-0.919</td>
<td>0.0985</td>
</tr>
<tr>
<td>12</td>
<td>-0.698</td>
<td>0.0464</td>
</tr>
<tr>
<td>14</td>
<td>-0.537</td>
<td>0.0207</td>
</tr>
<tr>
<td>16</td>
<td>-0.418</td>
<td>0.0076</td>
</tr>
<tr>
<td>18</td>
<td>-0.328</td>
<td>0.0009</td>
</tr>
<tr>
<td>20</td>
<td>-0.259</td>
<td>-0.0024</td>
</tr>
<tr>
<td>22</td>
<td>-0.207</td>
<td>-0.0040</td>
</tr>
<tr>
<td>24</td>
<td>-0.167</td>
<td>-0.0046</td>
</tr>
<tr>
<td>26</td>
<td>-0.135</td>
<td>-0.0046</td>
</tr>
<tr>
<td>28</td>
<td>-0.110</td>
<td>-0.0044</td>
</tr>
<tr>
<td>30</td>
<td>-0.091</td>
<td>-0.0041</td>
</tr>
</tbody>
</table>

With $\beta=0.56$, the EPG coefficients determined were: $a=5.076\times10^{-2}$ cm$^4$/atm, $b=0.2569$ and $c=2.689\times10^{-3}$. Using $a$, $b$ and $c$, the relaxation matrix $W_p$, the first order mixing coefficients, and the second order coefficients were calculated. Table 5.6 lists the first order mixing coefficients and compares the results to the measured coefficients. Table 5.7 lists the quadratic pressure shift coefficients and quadratic strength coefficients determined from the scaling analysis.
5.3.5 Line Mixing Sum Rules

In general, no matter what level of approximation, several sum rules must be satisfied (Pine, 1997a). These rules are summarised here:

I) \[ \sum p_i = \text{constant} \]

II) \[ \sum q_i = 0 \]

III) \[ \sum \gamma_i = \sum P\gamma_o^i \] \hspace{1cm} (5.18)

IV) \[ \sum \delta_i = \sum P\delta_o^i . \]

Equation I states that the total intensity of the band must remain constant and equal to the band intensity. In other words, the intensity transfers from one line to another line. Equation II requires that all the asymmetry components add to zero. Equations I and II are proven by Pine (1997a) using direct substitution for \( p_i \) and \( q_i \) with equation 2.15. Equations III and IV state that the total broadening and total shift are calculable from the values for isolated lines. These two properties follow directly from the fact that the trace of a matrix is invariant under diagonalisation.

The sum rule for line mixing coefficients (Strow et al., 1994; Pine, 1997b) in the Rosenkranz approximation is written, \[ \sum S_i \gamma_i = 0. \] We checked our experimental values for agreement with this sum rule and found \[ \sum S_i \gamma_i = 1.71 \times 10^{-22} - 1.37 \times 10^{-22} = 3.4(4) \times 10^{-23} \text{ cm}^{-1} / (\text{mol-cm}^2) \] which does not equal zero within error. The sums for the positive and negative contributions are shown separately. Since lines with \( J > 30 \) were not measured, the EPG law results were used for these line mixing parameters. However, because the line strengths for these lines were relatively weak, the sum was not overly sensitive to these values. If instead of the EPG law results, we assume that \( \gamma_{30} = \gamma_{30} \), the sum is \[ 2.0(4) \times 10^{-23} \text{ cm}^{-1} / (\text{mol-cm}^2) \]. The immediate consequence of this result is that either the sum rule does not hold or the error estimates for the mixing coefficients are too small. This is the only sum rule measurement of which we are aware. Pine (1997b) measured mixing coefficients in CH\(_4\) but constrained the mixing coefficients in the fit to satisfy this sum rule.

The proof of the sum rule is not rigorous in that it relies on detailed balance and the impact approximation. The impact approximation is a necessary assumption of the Baranger line shape, equation 2.15. This may have some bearing on these constraints, particularly equation II. This sum rule

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rule can be understood physically. At frequencies far from the band centre, the wings of the dispersion terms, which decay as \(1/v\), dominate over the wings of the Lorentz terms, which decay as \(1/v^2\). To ensure that the wings of the dispersion terms add to zero and do not create a region with negative absorption, this sum rule must be satisfied (Strow et al., 1994). However, such an argument fails because the impact approximation breaks down in the far wings of a line shape and the line shape is no longer Lorentzian or dispersive.

Additional sources of analysis error might also explain why the sum does not equal zero. The estimates of error for the individual coefficients were based on the linear least squares fit to the measured mixing coefficients which did not allow for the estimation of error due to systematic causes. There are two systematic sources of error which have not been included in the error estimate.

We have not yet offered any evidence to support the assumption that the relative shifting of the lines within the band has been ignored. The relaxation matrix can be used to provide some justification. It will be shown that the quadratic line mixing shift coefficients can be estimated from the relaxation matrix and are given in table 5.7. Except for the \(Q(2)\) line, all the lines should shift by about the same but negligible amount (less than -0.2MHz at 8kPa). The \(Q(2)\) line would be shifted by about +1.3MHz. There is no experimental evidence for a quadratic shifting of the \(Q(2)\) line relative to the rest of the band. However, since line shift and measured line asymmetry are highly correlated we cannot entirely rule out the possibility that we have confused some relative shifting of lines with line mixing.

Another concern is that the fits were analysed within the first order Rosenkranz approximation, which may not be correct within experimental accuracy. This possibility will be examined again in chapter 7 after we discuss higher order line mixing effects.

5.4 SUMMARY

In this chapter we have presented a first order line mixing analysis of spectra recorded at pressures under 11kPa. From the medium pressure spectra, several line and band parameters were measured. Most importantly we have shown through the measurement of the mixing parameters that (1) the spectra can be represented by the addition of a dispersive line shape associated with each line
and (2) the size of the dispersive component increases linearly with pressure.

Although we have calculated the relaxation matrix using the EPG gap law, the results of this calculation were used for comparison purposes only. It is important to note that the measured mixing coefficients are independent of gap law calculations, assumptions about the presence of vibrational dephasing, or structure of the relaxation matrix. As such they directly verify the accepted picture of line mixing as applied to this band.

The band strength and broadening coefficients measured here will be used for the analysis in chapter Higher Order Mixing Results. Before continuing with the analysis of these higher pressure spectra we must first discuss the speed-dependent model.
CHAPTER 6

SPEED-DEPENDENT PROFILE

6.1 SPEED DEPENDENCE

In this chapter we discuss speed-dependent line shape effects. Many unsuccessful attempts were made to fit the high pressure spectra before the current analysis procedure was developed. We will not discuss all the unsuccessful attempts here but simply state that the methods used to analyse the medium pressure spectra could not fit the high pressure spectra without significant structure in the residuals. It will be shown that the failure to include speed-dependence in the high pressure fits resulted in a larger residual which then coupled into other fitting parameters. An important step in the fitting of these high pressure spectra was the development of a speed-dependent line shape (the double hard collision line shape) in a form that was feasible to use on multi-line fits.

The reasons for considering speed dependence were drawn from similar observations in spectra of CO in N₂ (Duggan et al., 1993; 1995) where the non-linear increase in Dicke narrowing to compensate for speed-dependent effects had also been observed. Duggan et al. found that a speed-dependent model explained much of the behaviour observed in the experimental spectra. There were two reasons to suggest that speed dependence would be at least as significant in pure CO₂ as it was for CO in N₂.

In the case of a heavy active molecule in a bath of relatively light perturber molecules, the collision rate is largely determined by the faster moving light perturbers. Such a situation means that speed-dependent effects are minimal since the speed of the slower moving active molecule has little impact on the collision rate. The converse situation where the perturbing molecules are relatively heavy and the active molecule is light, creates a situation where the collision rate is directly related to the active molecule's speed and speed-dependent effects are expected to be important. Hence, the
active-to-perturber molecular mass ratio is important in determining the importance of speed-dependent effects and in both CO in N₂ and pure CO₂ the mass ratio is the same, 1:1.

Over a limited pressure regime the non-physical behaviour of the Dicke narrowing parameter, \( z \), compensated for the dominant speed-dependent effects. But the magnitude of the Dicke narrowing effect is limited by the size of Doppler component in the line shape. For \( z \gg 1 \) the hard collision line shape is essentially Lorentzian and further increases in the narrowing parameter will have little effect on the line shape. Because CO₂ is a heavier molecule than CO and thus has a smaller Doppler width and because the pressure broadening coefficient for pure CO₂ is larger than for CO in N₂, the contribution from the translational component is smaller in CO₂ than CO, for any given pressure. Thus, the hard collision model will fail to fit the CO₂ spectra at lower pressures than it fails for CO spectra.

All the line shape models discussed thus far are homogeneous in the internal line shape, in that they assume a single dephasing rate for all speed classes. We explicitly made this assumption when we discussed the hard collision model, where it was assumed that \( \Gamma(v) \) and \( \delta(v) \) were independent of velocity. A simple physical picture suggests that this clearly is not the case for \( \Gamma(v) \), since faster molecules are apt to collide more frequently than slower molecules. In fact the collision cross section is also a function of speed through the interaction potential. In the previous chapter we assumed both \( \Gamma \) and \( \delta \) to be speed independent and in doing so we disregarded what we shall refer to as speed-dependent effects. In this section we present a phenomenological approach to the inclusion of speed-dependent effects in the line shape model. We take a pragmatic approach to the inclusion of speed dependence since state-of-the-art models (Ciurltyo and Szudy, 1997; Duggan *et al.*, 1997; Robert *et al.*, 1993) require additional parameters and tend to be computationally time consuming.

A fully speed-dependent model requires that both the translational motion and collision rate be functions of speed. The common dependence on speed results in a coupling of the translational and internal motions which prevents the line shape from being represented as a convolution of the translational and internal line shapes. Because the phase changing collision rate, \( \Gamma(v) \), and the line shift, \( \delta(v) \), have an explicit speed dependence, the integral of equation 5.7 is generally intractable without assuming \( \Gamma \) and \( \delta \) to be speed independent.
We adapt the approach that Duggan et al. (1995) used to include speed dependence in the soft collision model, to include speed-dependent effects in the hard collision model. Based on the fact that the magnitudes of the pressure shifts are very small at the pressures we studied, we assume the effects of speed-dependent pressure shifts are negligible and only consider the speed-dependent effects of $\Gamma(v)$. We also ignore correlation between the internal and translational motion. Under these assumptions the hard collision model of Rautian and Sobelman (1967) (see equation 5.7) can again be separated into a convolution of two line shapes:

$$I(\omega) = \frac{1}{\pi} \int d\omega' \Re \left\{ \int d\bar{v} \frac{W_M(\bar{v})}{\Gamma(\bar{v}) - i(\omega - \delta - \omega')} \right\} \Re \left\{ \frac{1}{\pi} \int \frac{W_M(\bar{v})d\bar{v}}{\beta - i(\omega' - k\bar{v})} \right\} \frac{1}{\beta - i(\omega' - k\bar{v})} . \tag{6.1}$$

The line shape represents a sum of Lorentzian line shapes, of width $\Gamma(v)$, weighted by the Maxwellian distribution $W_M(\bar{v})$, convoluted with a translational line shape. Different than equation 5.7, in this equation the internal and translational parts are integrated separately over velocity and therefore the coupling is ignored. This line shape can therefore be represented by,

$$I(\omega) = \int W(\bar{v}) \cdot I(\omega, \Gamma(v)) d\bar{v} , \tag{6.2}$$

where $I(\omega, \Gamma(v))$ represents the speed independent Rautian and Sobelman hard collision model for a speed class $v$, as given by equation 5.8 (equation 6.3 of Rautian and Sobelman, 1967).

Equation 6.2 is impractical to implement into our analysis since we cannot analytically relate the integral to the complex probability function for computation. However, it can be approximated and written as the weighted sum of speed independent hard collision models, with an appropriate width for each speed class,

$$I(\omega) \approx \sum_j W(v_j) \cdot I(\omega, \Gamma(v_j)) . \tag{6.3}$$

Duggan et al. showed that 50 discrete speed intervals adequately represented the soft collision model for CO and the results were found to depend only weakly on the functional form of $\Gamma(v)$ (Duggan et al., 1995). Unfortunately, even a model with 50 speed groups is too computationally expensive for
Chapter 6: SPEED-DEPENDENT PROFILE - Speed Dependence

us to implement in a multi-line spectral analysis program.

Our approach simplifies this line shape further by using the sum of just two profiles. The line shape is therefore written as,

\[ I(v) = rI(v, \gamma_1) + (1-r)I(v, \gamma_2) \]  (6.4)

Note that the parameters \( r, \gamma_1, \) and \( \gamma_2 \) in this profile do not represent two actual speed classes but rather are empirically determined such that equation 6.4 best approximates equation 6.3. We refer to this profile as the double hard collision profile. Note that if the translational component is ignored then the same parameters will give a double Lorentz profile.

To determine the parameters \( r, \gamma_1, \) and \( \gamma_2 \) we fit the double Lorentz profile to a theoretical speed-dependent profile. We used the speed-dependent soft collision line shape of Duggan et al. (1995) to generate this theoretical profile. The translational contribution to the soft collision model was removed by setting the temperature to near zero and using a large collisional line width. A speed-independent model such as a Lorentz line shape is a function of a single width, \( \gamma_{Lor} \), which cannot be uniquely related to the speed-dependent widths, \( \gamma(v) \). Instead we define the weighted mean width, \( \gamma_{\text{mean}} = \langle W(\sqrt{v})\gamma(\sqrt{v}) \rangle \). The width used in the theoretical profile was \( \gamma_{\text{mean}} = 0.1 \text{cm}^{-1} \).

The theoretical profile was fit using equation 6.4. The following figure shows the results of the fits to this theoretical profile using both a single and a double Lorentz model. The double Lorentz model clearly gives a superior fit. The fit parameters of the double Lorentz fit are given in table 6.1. Importantly, the parameter \( r \) is pressure independent since pressure does not change the Maxwellian distribution \( W(\sqrt{v}) \) and since the speed-dependent widths \( \gamma(\sqrt{v}) \) scale directly with pressure so do the parameters \( \gamma_1 \) and \( \gamma_2 \).

It is important to note that the double hard collision model has the same number of free parameters as the single hard collision model, only one parameter for each the strength, \( p \), and the broadening, \( \gamma \). The parameters for the two profiles that sum to give the line shape were then calculated using the predetermined scaling factors, \( \gamma_1 = 0.9433\gamma, \gamma_2 = 1.3776\gamma, p_1 = 0.85623p, \) and
Table 6.1. Results of the fit of the double Lorentz model to the theoretical speed-dependent profile.

<table>
<thead>
<tr>
<th>Speed Group</th>
<th>Strength</th>
<th>Width (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group 1</td>
<td>(r=0.85623)</td>
<td>(\gamma_1=0.09433)</td>
</tr>
<tr>
<td>Group 2</td>
<td>1-(r=0.14377)</td>
<td>(\gamma_2=0.13776)</td>
</tr>
</tbody>
</table>

Because of their computational simplicity, these models ran relatively quickly.

When fit to the theoretical profile, the \(\gamma_{\text{Lor}}\) that gives the best approximation of a single Lorentzian to a sum of Lorentzians profile was found to be \(\gamma_{\text{Lor}}=0.09877\text{cm}^{-1}\). Hence, \(\gamma_{\text{Lor}}\) is smaller than \(\gamma_{\text{mean}}\) for nearly equivalent line shapes.

What we have presented here is not a rigorous development of the physics but rather a justification for a model - which does not introduce any extra free parameters - that will be shown to improve the fits to the data. Admittedly the model fails to deal with the effects of correlation between the translational and internal line shapes and its derivation relies on the approximate line shape of Duggan et al. (1995).
Figure 6.1. Theoretical speed-dependent fit. The profile (-----) was calculated from the line shape of Duggan et al. (1995) with a weighted line width of $\gamma_{\text{mean}} = 0.1 \text{cm}^{-1}$ and a relative strength of 1. The residuals of the Lorentzian (- - -) and double Lorentzian (-----) fits to the line shape are shown with significant scaling factors of 100 and 2000 respectively.
6.2 SPEED-DEPENDENT FITS

Figures 6.2 and 6.3 compare two spectra analysed with both the single and double hard collision models. The details of the fitting and the results of the fits will be discussed in the next chapter. The superior quality of the double hard collision fits is immediately apparent in the residuals. Fitting spectra at these pressures requires spectra with excellent signal-to-noise ratios. However, if the line shape model cannot fit the spectra, then the quality of the data is not fully utilised. The residuals in figures 6.2d and 6.3d show the potential for the structure due to speed dependence to couple into the other fitting parameters.

The narrowing parameter has effectively compensated for these speed-dependent effects below 11kPa. Hence, in terms of measuring first order line mixing coefficients there is little to be gained from fitting medium pressure spectra with the double hard collision model. Work by Sinclair et al. (1997) has shown that the measured broadening coefficients are directly affected by the line shape model used. Because the double hard collision model is empirical, it makes the broadening coefficients determined difficult to relate to theory and of limited value except when used with this model.

Note that Strow and Pine (1988) used a difference frequency spectrometer to measure a N$_2$O $Q$-branch and were able to fit 13kPa (100Torr) spectra within error with a Lorentz line shape. They saw no need for a speed-dependent profile and concluded that Dicke narrowing had completely narrowed the translational effects. In fact speed-dependent effects were not observed in their spectra at pressures up to one atmosphere. We believe our requirement for speed-dependent profiles results from our higher signal-to-noise ratios and the fitting requirements of our analysis.
Figure 6.2. Comparison of single and double hard collision models: a) 32.5kPa spectrum; b) residual from full relaxation matrix inversion with single hard collision model; c) same as (b) with double hard collision model; d) same as (b) but fit for the strengths of the line components; e) same as (d) but with a double hard collision model.
Figure 6.3. Same as above but with 59kPa spectrum.
6.3 SPEED-DEPENDENT LINE MIXING

As far as we are aware, speed dependence has never been included in a line mixing formulation. Here we just present a short explanation of the approach we considered and the pitfalls that must be overcome before a rigorous implementation of speed-dependent line mixing could be developed.

Equation 5.6 might suggest that a time domain representation of speed-dependent effects on the isolated (symmetrical) line shape would naturally lead to a means for calculating the speed-dependent effects on the asymmetric component. In the case of the speed-dependent hard collision model given in equation 5.7, the asymmetric component would be given by the imaginary component within the braces. Earlier we justified the application of equation 5.6 because the speed-independent hard collision model could be represented as the convolution of a Lorentz line shape and a second symmetric line shape. However, this necessarily assumed $\Gamma$ and $\delta$ to be independent of velocity. Hence it is unjustifiable to use equation 5.6 to calculate the asymmetry component for the speed-dependent hard collision profile.

There is a second problem with calculating the speed-dependent line mixing component which can be shown for the case where translational effects are ignored. The problem arises because the relaxation matrix off-diagonal elements will also be speed-dependent. Because the inelastic collision rates (half widths) are speed-dependent, the diagonal relaxation matrix elements are speed-dependent, $\gamma(v) = W_f(v)$. Since the off-diagonal elements are related to the diagonal elements through a sum rule, the off-diagonal elements must necessarily also be speed-dependent. Therefore the entire relaxation matrix is speed-dependent, $W(v)$.

We can rewrite Baranger's line mixing equation in an inhomogeneous speed-dependent form integrated over speed classes:

$$ k(v) = \frac{N}{\pi} \int_{0}^{\infty} W_M(v) \text{Im} \left\{ \bar{\mu}^\dagger \left[ v I - v_o - i P W(v) \right]^{-1} \rho \bar{\mu} \right\} dv \, . \quad (6.5) $$

Within the Rosenkranz approximation the speed-dependent profile can be written as,

$$ I(\omega) = \int W_M(v) \left[ I_{\text{sym}}(\omega, \Gamma(v)) + Y(v) \cdot I_{\text{asym}}(\omega, \Gamma(v)) \right] dv \, , \quad (6.6) $$
where the $Y(y)$ is speed-dependent because,

$$Y(v) = 2 \sum_{j} \frac{\mu_j}{\mu_i} \frac{W_j(v)}{v_i-v_j} \quad (6.7)$$

Thus each speed class has not only an associated width, $\Gamma(v)$, but a speed-dependent line mixing coefficient, $Y(v)$. Faster speed classes will not only have a larger width but have a larger asymmetry. This is in contrast to equation 5.6 which does not predict the speed dependence of the line mixing coefficient. We have only examined the speed dependence of line mixing within the Rosenkranz approximation, however, it shows that equation 5.6 is not generally applicable to speed-dependent profiles.

*Line-Fit* contains two, speed-dependent models, A and B, which make different assumptions about the speed-dependent nature of line mixing. Model A includes speed dependence in the asymmetry as it does for the symmetric component. It uses the sum of two asymmetry terms with widths $\gamma_1$ and $\gamma_2$ and strengths $q_1$ and $q_2$. The parameters $q_1$ and $q_2$ were determined by forming the sum of speed-dependent dispersion line shapes. Model B ignores the speed dependence of the asymmetry and uses a single asymmetry term with width $\gamma$ and strength $q$. Since no significant difference was ever observed by using either model A or B, model A was used whenever a speed-dependent profile was required.
CHAPTER 7

HIGHER ORDER LINE MIXING

At high pressures the individual $Q$-branch lines blend significantly and the line mixing effects are large. The effects of the translational component of the line shape are now less important because the collisional widths are much larger than the translational widths. Because the line shapes severely overlap in this region, it becomes increasingly difficult to extract individual line shape parameters from the fits. But, by appropriate constraint of the fit parameters it is still possible to fit high pressure spectra. Fits are further complicated because first order line mixing is no longer sufficient to fit the data.

The high pressure spectra are particularly interesting to study since we expect significant line mixing effects to be evident. The nonlinear pressure dependence of the parameters makes the analysis less certain than at low and medium pressures where the pressure dependence is better understood. We will show that, using a speed-dependent model and fitting for the strengths of the individual absorption lines we have achieved good, physically meaningful fits to the spectral data. Before continuing with the analysis of spectra we will first examine the expected behaviour of the line shape parameters as a function of pressure.
7.1 EPG RELAXATION MATRIX INVERSION

To examine the line shape effects of the full EPG relaxation matrix as a function of pressure we could generate spectral profiles for a range of pressures as has been done by Gentry and Strow (1987), Lavorel et al. (1990a; 1990b), and Hartmann and L’Haridon (1995). However, it is more enlightening to look at the individual line shape parameters as a function of pressure, remembering that line mixing (higher than first order) affects only the line shape parameters, not the basic line shape.

The Theory chapter described diagonalisation of the relaxation matrix using eigenvalue decomposition. The diagonalisation was performed using a matrix manipulation package known as RLAB. Because RLAB gives no predefined order to the eigenvalues, the eigenvalues and associated eigenvectors were sorted into ascending order by the size of the real parts of the eigenvalues. Substituting the eigenvalues and eigenvectors into equation 2.15 gave the line frequencies, half widths, symmetric line strengths and asymmetric line strengths. The parameters were calculated over a range of pressures between 0.01 and 10 atmospheres using the EPG relaxation matrix calculated earlier with $\beta=0.56$. In each case higher J lines are not shown. The behaviour of these lines is, in general, very similar to the highest J line shown.
Figure 7.1. Frequencies of the $Q$ branch as calculated from inversion of the EPG relaxation matrix. The $\Lambda_i$ are the eigenvalues. The solid lines show the pressure dependence of the $Q$ branch positions as calculated from the inversion of the EPG relaxation matrix. The lower panel is an enlargement of the behaviour below two atmospheres. The dotted lines show the second order approximation of Smith (1981).
Figure 7.1 shows the line positions for lines $Q(2)$ to $Q(16)$ as a function of frequency. The line positions are given by the real parts of the eigenvalues, in ascending order with the following exception: the assignment of eigenvalues must flip if the centre frequencies of the two lines shift far enough to intersect. For example: the $Q(10)$ line starts as the fifth eigenvalue, $\Lambda_4$, but after crossing $Q(8)$ it becomes the fourth eigenvalue, $\Lambda_4$. The assignments are verified by the similarity of the eigenvectors, i.e. the line strengths are continuous functions of pressure with these assignments.

The line positions show a complex behaviour as a function of pressure. The $Q(8)$ line is particularly interesting in that it migrates across the band towards higher frequency. Figure 7.1 also includes the simple quadratic pressure shift (equation 2.19) predicted by the approximation of Smith (1981). As expected, this second order expansion is valid only at pressures below a certain limit. What is surprising is that the second order expansion becomes invalid at pressures as low as 0.5 atmospheres for the $Q(2)$ and $Q(4)$ lines.
Figure 7.2. Pressure dependence of the symmetric strength component calculated from the inversion of the relaxation matrix. Shown are the Q(2) to Q(12) lines. The solid lines show the pressure dependence of the $Q$ branch line strengths as calculated from inversion of the relaxation matrix. The lower panel is an enlargement of the behaviour below two atmospheres. The dotted lines show the second order approximation of Smith (1981).
Chapter 7: HIGHER ORDER LINE MIXING - Relaxation Matrix Inversion

The results of the full inverse model for the symmetric strength component, $p_n$, were equally interesting and complex. Figure 7.2 shows the symmetric strength component versus pressure. At 0.2 atmospheres the strength of the $Q(2)$ line has noticeably decreased. Because the total strength of the band must be conserved, the strengths of the other lines, notably $Q(4)$ and $Q(6)$, increase to compensate. At approximately one half atmosphere the strength of the $Q(2)$ line actually becomes negative. At first this might appear unphysical as a negative line strength implies a positive gain to the transmitted radiation, i.e. $\tau > 1$. However, this never occurs since $Q(2)$ cannot exist in isolation and the transmission from the sum of all lines remains less than or equal to unity. The exchange of line intensity is most apparent between the $Q(6)$ and $Q(8)$ lines near two atmospheres. This large exchange occurs because at this pressure the lines are extremely close to each other as can be seen in figure 7.1.

The $Q(8)$ line eventually becomes the dominant line and acquires the line strength of the entire band. At very high pressures the $Q(8)$ line will be the only line of appreciable strength and will in fact represent the transmission profile of the entire band. Since lines $Q(6)$ and $Q(8)$ approach very closely before they start to diverge, it is interesting to speculate that under slightly different conditions the $Q(6)$ line might be the dominant line.

Smith (1981) predicts a quadratic pressure dependence of the symmetric line strength, $p_n$ (equation 2.20). Figure 7.2 shows the quadratic strength component with the full inverse calculation. As with the quadratic pressure shift, this approximation is only valid over a limited pressure region. There is reasonable agreement until 0.4 atmospheres, above which the deviations become quite significant.
To complete the picture of the collapsing band as a function of pressure we will now look at the behaviour of the broadening coefficients, $\gamma^0$, and asymmetric strengths normalised to one atmosphere, $q^0$, both of which are predicted to remain constant in Smith's second order expansion. Figure 7.3 shows the pressure dependence for lines $Q(2)$ to $Q(12)$. Again the second order theory breaks down with the $Q(2)$ broadening coefficient deviating from constant at about 0.4 atmospheres. Note that the $Q(8)$ broadening coefficient starts to decrease significantly at pressures over 1.5 atmospheres. The pressures at which the $Q(8)$ line narrows correspond to the same pressures over which the $Q(8)$ line becomes dominant in line strength. This effect is what some authors refer to as motional narrowing (Dion and May, 1973). At sufficiently high pressures the entire $Q$-branch
becomes a single Lorentzian line with a width that decreases with pressure (neglecting the effects of collisions other than rotationally inelastic collisions).

The line mixing strengths normalised to one atmosphere, $q^\beta$, as a function of pressure are shown in figure 7.4. The high order line mixing effects are rich in structure and become quite pronounced above 0.4 atm. Note that the variation in asymmetrical strengths is independent of the symmetric strengths. In particular, the $Q(2)$ asymmetric strength remains positive even when the strength of its symmetrical component is zero or negative. The interplay between lines $Q(6)$ and $Q(8)$ is again evident in the mixing behaviour of these lines. Remember that the sum rule for the mixing parameters states that $\sum q_i = 0$. Above two atmospheres the $Q(8)$ line has the only positive line

![Figure 7.4. Pressure dependence of the line mixing strengths normalised to one atmosphere, $q^\beta$, calculated from the inversion of the relaxation matrix. Shown are the $Q(2)$ to $Q(12)$ lines.](image)
mixing parameter, $q_s$, and so must equal the sum of all the lines with negative line mixing, but note that not all the lines included in the sum are shown in figure 7.4. Eventually, $q_s$ goes to zero, since the final, symmetrical, collapsed band is represented by the $Q(8)$ line.

This line-by-line picture of the evolution of the band is very useful for gaining insight into the relevant changes induced by line mixing. It illustrates the pressure regions where the Rosenkranz and Smith approximations are valid and where they are definitely invalid. It also shows how a band transforms from being represented by a sum of lines to a representation with just a single line.

### 7.2 HIGH PRESSURE FITS

Based on the results from the relaxation matrix inversion we expect to observe higher order line mixing effects in the high pressure regime we defined. We will show that it was possible to measure the pressure dependence of the symmetric line strengths from fits to the data. Such measurements confirm the picture of the collapsing band and give indirect verification of the off-diagonal elements of the relaxation matrix.

Figures 7.5 and 7.6 show two higher pressure spectra with several residuals. For each of the residuals, the synthetic spectrum was calculated on a line-by-line basis using the double hard collision model. The first residuals, (b), are based on the differences between the experimental spectra and the Rosenkranz first order approximation. The second residuals, (c), are similar but the synthetic spectra were calculated using Smith's second order equation. The first order mixing coefficients, and the second order quadratic shift and quadratic strength parameters were calculated in chapter 5 and are list in tables 5.6 and 5.7. Residuals (b) and (c) are much larger than the experimental noise, but the inclusion of second order effects has clearly reduced the size of the residuals. The dominant source of residual in (b) is almost certainly the breakdown of the Rosenkranz approximation. There are two
explanations for the residual structure in (c): one explanation is that the line parameters are inaccurate; the second explanation is that the second order approximation is inaccurate at these pressures.

To test the validity of the second order approximation the third residual, (d), shows the difference between the experimental spectrum and the spectrum calculated from the full inversion of the relaxation matrix. For each spectrum at the known pressure, the initial values for the line widths, line positions, line strengths and mixing strengths were generated from equations 2.15. Two adjustments were then made to the results. The resulting line strengths and broadening coefficients were adjusted to agree with our medium pressure measurements. Because we earlier measured the band strength to be 0.97 of the HITRAN96 band strength and we used HITRAN96 line strengths for the calculation of the relaxation matrix, all line strengths resulting from the matrix inversion were multiplied by 0.97. As was shown in figure 5.13, the EPG scaling law fit of the relaxation matrix diagonal elements to the measured broadening coefficients did not reproduce the broadening coefficients within error. Attempts to directly apply the broadening coefficients calculated from the relaxation matrix inversion were unsuccessful. Instead we used only the calculated change in the line widths from their low pressure values. The following equation explains the correction,

\[ y'(P) = P y_{0} + \left( \gamma'_{\lambda}(P) - P \text{Re}[W_{ii}] \right) \]

where \( y_{0} \) are the measured broadening coefficients, \( W_{ii} \) are the relaxation matrix diagonal elements, \( \gamma'_{\lambda}(P) \) are the line widths calculated by the inversion process, and \( y'(P) \) are the line widths used to calculate the line-by-line synthetic spectra. Note that an equivalent method would have set the diagonal elements of the relaxation matrix equal to the measured broadening coefficients.
Figure 7.5. Spectrum at 32.5 kPa with residuals: b) Rosenkranz's first order approximation, c) Smith's second order approximation, d) inversion of full relaxation matrix, e) same as (d) except the symmetric strengths of the line components were fit.
The inclusion of higher order line mixing effects through the use of the full inverse model actually made the residual (d) larger than (c). Such results clearly show that residuals (c), resulting from the quadratic model of line mixing, cannot simply be explained by the absence of higher order line mixing effects and we must question the accuracy of the parameters calculated from the estimated
relaxation matrix.

In an effort to quantify the differences between the observed and calculated spectra, we fit our model to the observed spectra. The parameters with the greatest uncertainty are those governing the first and second order line mixing effects, \(i.e.\) the mixing, the quadratic shift and the quadratic strength coefficients.

The asymmetric strengths, \(q_n\), clearly have an important impact on the fits at these pressures. The \(Q(2)\) asymmetry component is actually stronger than the symmetrical component at pressures greater than 35kPa. However, we have directly measured the mixing coefficients at medium pressures and the relaxation matrix does to a good degree reproduce the first order mixing coefficients. This does not assure that the relaxation matrix will produce accurate higher order mixing strengths but, at least to second order, the mixing coefficients are constant.

Even at the highest pressures we considered, figure 7.3 suggests only a weak pressure dependence of the broadening coefficient due to line mixing. Thus, the predicted line widths are essentially the isolated line shape line widths which were measured at medium pressures and which we believe to be very accurate. Note that the Lorentz scaling factor was fit to allow for an overall adjustment of the line widths. This was necessary since we were using a different line shape model, the double hard collision model, which has a systematically different line width than the hard collision model.

No measurements exist for frequency shifts caused by higher order line mixing. The predicted shifts due to line mixing (table 5.7) are at most 10\% of the half widths for pressures less than one atmosphere and small errors in these shifts should have a limited effect on the band shape. Errors in these shifts are most likely to couple into the shift of the overall band which can be measured directly from the spectra.
Because the lines within the higher pressure spectra were highly blended, the number of free parameters to be fit needed to be reduced to a minimum. Ultimately, we chose to fit the symmetric line strengths and to fix the asymmetric strengths, half widths, and relative line frequencies at their calculated values. In addition, the baseline and the Lorentz width scaling factor were fit and the narrowing coefficient was fixed at 10 atm\(^{-1}\). The initial values for the fixed line shape parameters were calculated at the appropriate pressure from the relaxation matrix inversion. By fitting for the individual line strengths we directly measured the intensity transfers, which to our knowledge has never been done before.

Unfortunately, many of the early spectra were contaminated by small amounts of air leaking in with the CO\(_2\). The air content changed the line widths and strengths sufficiently that extra fitting parameters were required in the fits. Therefore the described fitting procedure was only applied to the spectra taken on Aug. 28 and Aug. 29, 1996. We will, however, describe the fits of a few spectra which were contaminated with air.

The residuals (\(e\)) resulting from fits at two pressures are shown in figures 7.5 and 7.6. The dramatic improvement in agreement between synthetic and measured spectra as a result of the fit is evident in the residual which is now \(\times 100\). Some small structure is still visible and there seems to be a line to line correspondence between the residuals and the spectra.

The results of the measured line strengths as a function of pressure are shown in figure 7.7. At the lowest pressures the line strengths are close to the line strengths for isolated lines but as the pressure increases, changes in the line strength can be observed. Perhaps the most interesting observation is that the \(Q(2)\) line strength dramatically decreases, at 60kPa becoming zero and at 72kPa the line strength is negative. Remember that in these fits the asymmetric contributions are quite large and although the \(Q(2)\) symmetric line strength may be zero, the
Figure 7.7. The measured strengths of the symmetric line shape components, $p_o$, as a function of pressure. Symbols show the measured values and the lines show the values predicted by the relaxation matrix.

Also plotted are the line strengths calculated from the relaxation matrix inversion. The differences between the measured line strengths and the predicted line strengths shown in figure 7.7 are sufficient to account for the dramatic reduction in the residual that is evident in figures 7.5 and 7.6. This figure shows that the relaxation matrix generally overestimates the intensity transfer at these pressures. For example, at pressures up to 55kPa the measured line strengths of the $Q(6)$ and $Q(8)$ lines show much less intensity change than the relaxation prediction.

Additional results for the $Q(2)$ line can be seen in figure 7.7 below 20kPa. These fits were performed on medium pressure spectra already analysed in chapter 5 and other spectra taken at approximately the same time. These spectra are not of the same quality as the other spectra analysed.
in this chapter. The baseline drifts are larger and there are small amounts of contamination by air in the cell. Still the intensity transfer can be seen even at 10kPa. The mixing ratio of air was based on a measurement of the band strength and then set as a fixed input parameter. Only the strengths of the $Q(2)$ and $Q(4)$ lines were fit for these spectra. The results below 20kPa agree well with the predicted intensity transfer and would be well modelled by Smith's (Smith, 1981) quadratic pressure dependence of the strength.

Since these medium pressure spectra show observable intensity transfer, we must question the Rosenkranz analysis used in chapter 5. To repeat the analysis of chapter 5 would require fitting for the strengths as well as the many other parameters we fit for at medium pressures. Unfortunately, only with the quality of the most recently taken spectra does this seem possible. More medium pressure spectra are thus required to perform such an analysis.

A critical view of the analysis performed would question the physical reality of the fits. We fit multiple parameters to spectra which actually show very little structure at high pressures and clearly we cannot be sure that the measured line strengths are unbiassed by error in the values of the fixed parameters. The implicit assumption in this fitting procedure is that the relaxation matrix and hence the initial parameters are approximately correct and we are simply measuring a small deviation from the expected behaviour. However, by fixing so many parameters we could be biasing the results of the fits. Evidence supporting the realism of the fits can be found in the physically meaningful behaviour of other fit parameters. The fact that the other parameters behave as expected, suggests that the spectra are not simply fit by a model with too many degrees of freedom, and conversely does not suggest that the constraining of the fixed parameters has forced the fit parameters to compensate in a non-physical manner.

As mentioned before, other fitting methods were also tested. Similar fits were performed with
the line strengths fixed and the asymmetries fitted. The resultant $\chi^2$ was increased by a factor of 3 with an associated increase in the size of the residual over the results where the strengths were fit. Furthermore, the resulting line mixing parameters appeared to be unphysical, bearing little resemblance to the expected values. Fitting both the asymmetries and the line strengths was also done but this made little improvement over fitting the line strengths alone.

The Lorentz width scaling factor is plotted versus pressure in figure 7.8 for fits using both the double hard collision model and the hard collision model. Some pressure dependence is evident for the double hard collision model, but except for the highest pressure the maximum deviation from unity is only approximately 0.5%. The hard collision model results show less change with pressure.

![Figure 7.8. The Lorentz scaling factor determined from fits. The diamonds are results from a double hard collision model and the triangles are results from the single hard collision model.](image)

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but are uniformly low by approximately 1%. The difference between the two models was expected since the results of the previous chapter predict the ratio of the half widths for the hard collision model and the double hard collision model to be 0.987.

Our broadening coefficients were determined with the hard collision model at medium pressure. We would therefore expect the Lorentz scaling factor to be unity for medium pressure spectra. The 6.6kPa spectra analysed with the hard collision model were offset from unity by more than 1%. The reason that the 6.6kPa hard collision results are offset is due to the fact that the narrowing coefficient was fixed at 10 atm$^{-1}$ and the Lorentz width compensated by being smaller. In our previous analysis at medium pressures, we fit the Dicke narrowing parameter which compensated for the narrowing associated with speed dependence. The fact that the difference in the definition of widths between the double hard collision and hard collision models corrects so well for the absence of Dicke narrowing at 6.6kPa appears to be purely coincidental. With so many other effects competing in the spectra studied here it is difficult to make definitive conclusions about the relationship between the double hard collision model and the hard collision model.
Figure 7.9. Measured shifts of spectra with reference to a 0.94kPa spectrum.

Unweighted regression forced through zero giving a band shift of

\[ \delta_0 = -49.5(3.6) \text{MHz/atm}. \]

The frequency offset of the band can be used to determine the linear pressure shift of the band as we did with the medium pressure results. After correction for the Fabry-Perot order number, the shifts of the band are clearly evident as shown in figure 7.9. The error bars were determined from the fits to the spectra and do not include small experimental frequency errors, which may affect the lowest pressure points, or errors in the fixed parameters, such as the asymmetry. We performed an unweighted regression through the points since the actual scatter about the line was larger than the estimated errors. The linear shift was measured to be -49.5(36)MHz/atm \((1.65(12) \times 10^3 \text{cm}^{-1}/\text{atm})\) which agrees within error with the linear shift measured at medium pressures to be -46(2)MHz.

Although this agreement is good, the measured shifts for spectra greater than 45kPa deviate from the
best fit line by as much as 10MHz (3×10^4 cm⁻¹). This is still a very small error considering that the band shows little structure on even a 3GHz (0.1 cm⁻¹) scale.

The baseline factor, \( B \), results are plotted versus pressure in figure 7.10. Although \( B \) is very close to unity for 6kPa spectra, the tendency is for it to decrease with pressure. This is consistent with the reasons for introducing \( B \). As the pressure increases, the wings of other lines not included in the synthetic spectra become stronger and have a larger effect. The effect of these wings is to increase the absorption and thus lower the transmission.

Line-by-line calculations of all CO₂ lines not explicitly included in the fits were performed.

![Figure 7.10. The baseline factor, \( B \), found by fits to spectra. The decrease in \( B \) represents the increase in the effect of wings of lines not included in the synthetic spectra.](image)
These calculations confirm that the transmission spectrum from the wings of these lines is nearly constant over the frequency range we studied. However, the quantitative transmission predicted by these calculations strongly depends on the number of lines included in the line-by-line calculation. Including all Hitran96 CO$_2$ lines between 1800 and 2400cm$^{-1}$ overestimates the absorption by a factor of 10. Since the line-by-line calculation uses a Voigt profile for the line shape and CO$_2$ is well known to be sub-Lorentzian in the far wings it is not surprising to find that such a calculation drastically overestimates the absorption (Hartmann and Boulet, 1991). The same calculation when limited to including lines between 2055cm$^{-1}$ and 2095cm$^{-1}$, underestimates the absorption by a factor of 4. Although we have not shown the measured offset to be correct, it seems plausible based on our knowledge of the CO$_2$ spectrum since it is a small effect and we assume it has not coupled into the fits in a strong or inconsistent way.

7.3 DISCUSSION of the RESULTS

We have shown that spectra up to 72kPa can be fit extremely well with a line-by-line model when line mixing and speed-dependent effects have been accounted for. The EPG law was used to calculate the line mixing effects with the exception of the intensity transfer between lines which was measured from the spectra. Small differences between the measured and predicted intensity transfer accounted for the differences between the measured spectra and the spectra predicted by the EPG law. The level of fit we achieved was only possible through the use of the double hard collision model to account for the speed-dependent line shape effects.

The results highlight the limits of a line-by-line calculation for high accuracy atmospheric transmission calculations. An examination of the higher order effects as predicted by the relaxation matrix such as was performed in this chapter would at the very least alert the user as to the limits of
the first or second order assumptions. For bands with lines more widely spaced, the first and second order effects are probably more than sufficient for pressures below one atmosphere. It is feasible to include line mixing into a line-by-line calculation with first order mixing, quadratic pressure shifts, and quadratic strength dependent terms. However, based on the complexity of the pressure dependence it would be exceedingly difficult to continue with a parametrisation of yet higher order effects.

Based on the EPG law calculation of chapter 5, the relaxation matrix was only verified in that it had the correct diagonal elements and it gave approximately the correct first order mixing coefficients. Given the size of the matrix, these criteria poorly constrain the off-diagonal elements of relaxation matrix. The direct measurements of intensity transfer presented in this chapter in fact verify to some extent the picture we drew of the collapsing band. This provides evidence that the off-diagonal elements are approximately correct. With further work it may be possible to use direct measurements of higher order mixing properties to help calculate the relaxation matrix.
CHAPTER 8

SUMMARY and CONCLUSIONS

Our goal was to make direct measurements of line mixing in a CO$_2$ $Q$-branch which, because the lines are very closely spaced, is both an experimentally and analytically challenging problem. We needed to acquire spectra of extremely high frequency resolution and good signal-to-noise, and to take full advantage of the quality of the data we also needed a line shape model which would fit the spectra within error. We have achieved our goal and in doing so have developed a new line shape model. Aside from measuring line mixing effects, other line shape parameters of interest have also been measured.

The experimental spectra were taken using a difference frequency spectrometer which was improved to the point where baseline spectra would drift by less than 1 part in 1000 across a 1.3cm$^{-1}$ scan. The signal-to-noise was in excess of 2000:1 and the frequency resolution was 1.5MHz ($5 \times 10^{-5}$cm$^{-1}$). Using this system, CO$_2$ $v_1+v_2$ $Q$-branch spectra were taken at 301K over a range of pressures up to 72kPa.

Line mixing effects were included on a line-by-line basis, which in its most general form is exactly equivalent to the band shape representation. To the line-by-line representation I added translational effects by using the hard collision model of Nelkin and Ghatak (1964), modified to
include an asymmetry term. This model represented the sum of a Lorentzian and a dispersion line shape convolved with a translational line shape that included Doppler broadening and Dicke narrowing effects. This model was included in a computer program written to fit the acquired spectra. From the fits, the line shape parameters were determined.

The most general line-by-line representation of Baranger (1958b; Levy et al., 1992) can be approximated to first order (Rosenkranz, 1975) or second order (Smith, 1981). We have considered both approximations in the analysis. Based on the Rosenkranz first order mixing analysis, several conclusions can be made. The spectra calculated using the first order parameters estimated by the EPG law of Strow and Edwards (1992) do not fit the measured spectra within error. This result was not surprising since Gentry and Strow (1987) had also noticed differences between predicted and measured spectra for the same band. However, at the start of this research it was unclear whether or not the discrepancy was due to some inaccuracies in the broadening coefficients, the band strength, and/or the line shape model. We can now state that even with the improved line shape model and the line parameters we measured, the EPG law still fails to give a relaxation matrix that fits the spectra.

The first order Rosenkranz mixing coefficients were measured directly from the spectra. They do not agree, within error, with the first order coefficients determined by the process above; note that the agreement for the Q(2) line only resulted from the appropriate selection of the free parameter, \( \beta \). The qualitative agreement between the mixing coefficients was, however, quite good. Given that these are the first direct measurements of first order line mixing in a band with such closely spaced lines, this level of agreement alone is a success. The best value of \( \beta \) was found to be 0.56 which gives a slight preference for collisionally induced rotational changes between even-even over even-odd rotational levels. Strow et al. (1994) found a value of 0.54. Note that our value was based on giving best agreement with the Q(2) mixing coefficient, whereas Strow et al.'s value was based on giving...
an overall best fit to the spectra.

The first order line mixing parameters calculated from the EPG law must satisfy a sum law which states that the first order mixing coefficients, weighted by the line strengths, sum to zero. Our mixing parameter measurements were not similarly constrained. In fact our measured first order line mixing parameters were found not to obey this rule within experimental error. We discussed the potential reasons for the disagreement within the Discussion of First Order Mixing Results. One distinct possibility is that a first order analysis may not be sufficiently accurate at any pressure to satisfy this sum law. We must point out that with the line shape model we used, the failure of the sum law means that these mixing coefficients will lead to a non-physical negative absorption at frequencies much lower than our $Q$-branch frequency and excessive absorption at higher frequencies.

Line mixing effects were also measured in spectra at pressures up to 72kPa. Over this pressure region the Rosenkranz first order line mixing approximation was not accurate and it was necessary to include higher order line mixing effects. It was also necessary to include the double hard collision model to account for speed-dependent line shape effects. The spectra were fit for the band shift, the baseline, an overall line width scaling factor and individual line strengths. With these parameters the spectra could be fit to a high degree of accuracy with little observable structure left in the residual. This was not possible using the hard collision model. The baseline and scaling factor determined from the fits were physically meaningful, which suggested these parameters were coupling to the fit in a physical manner. The measured line strengths displayed strong line mixing effects. Most notably a negative line strength was measured for the $Q(2)$ line. The line strengths versus pressure were compared to the strength dependence predicted by the EPG law and had qualitatively similar behaviour. Small differences in the strengths did however account for considerable differences in the observed residuals.
These measurements of intensity transfer are unique. They are a major step towards measuring higher order line mixing effects which may in turn give more information about the off-diagonal relaxation matrix elements. As mentioned by Thibault et al. (1992a), only a complete measurement of the state-to-state rates will completely verify a relaxation matrix estimation. But these measurements verify in a manner different than previous studies, the accuracy of the EPG law method for calculating the relaxation matrix. They also show that issues such as Dicke narrowing and speed dependence are observable and important in a densely mixed band such as this.

As already stated, the spectra at pressures less than 11kPa were analysed within the Rosenkranz first order approximation of line mixing. From these measurements the following parameters were measured: the Lorentz broadening coefficients, the first order mixing coefficients, the narrowing parameters, the band strength, and the band shift. The parameters for individual lines were determined for lines $Q(2)$ to $Q(30)$.

With the exception of a few $Q$-branch lines reported by Gentry and Strow (1987) our measurements are the only CO$_2$ $Q$-branch line width measurements published (Berman et al., 1997). We have argued that although the $Q$-branch line width measurements are much more difficult to make, they are of equal or better accuracy than measurements of other groups’ $P$- and $R$-branch measurements. Our measurements confirm for this band what was previously assumed: the line widths have little or no dependence on the vibrational transition or branch.

The band strength has been measured before but our measurement of $4.03(2)\times10^{-21}\text{cm}^{-1}/(\text{mol}\cdot\text{cm}^2)$ differs from the currently accepted Hitran96 value (Rothman et al., 1992) by 3% which is outside the errors bars of either measurement. Our measurement is in closer agreement with the work of Gentry and Strow (1987) and Arcas et al. (1982).

The band shift was measured within the Rosenkranz approximation at pressures below 11kPa.
and using a full line mixing model at pressures up to 72kPa. The two values were consistent with each other, however, because the higher pressure measurement was more sensitive to errors caused by line mixing effects we just quote the medium pressure value -46(2)MHZ/atm (-1.53(6)×10^{-3}cm^{-1}/atm). Thus we can state with confidence that the linear pressure shift is non-zero, showing the theory of Thibault et al. (1992b) to be incorrect. Other groups have measured $Q$-branch shifts of other bands and molecules and they all find the shift to be negative, although there is little agreement amongst the values. It is unusual to measure the line shift at pressures as low as we have since the absolute shifts are very small. Most measurements are made at pressures of several atmospheres and are more susceptible to errors introduced by line mixing effects. Our measurement should reduce any such effects.

Physically significant narrowing parameters could not be determined from the fits because the Dicke narrowing displayed a strong non-linear pressure dependence. Although we suspect the non-linearity was in part due to inadequacies of the hard collision model, it was assumed that it resulted predominantly from speed-dependent effects, unaccounted for by the hard collision model, coupling to the narrowing in the fits.

The hard collision model fit the spectra within error at pressures less than 11kPa, however the fits relied on unphysical narrowing parameters. At pressures higher than 11kPa the hard collision model could no longer fit the data regardless of the narrowing parameter value. This led to the inclusion of speed-dependent effects into the line shape model through the double hard collision model.

The analysis of a very dense spectral region has been undertaken with a large degree of success. For this analysis to have been successful a host of line shape effects were included, each of which alone is an area of study. Aside from the results for this particular band, we have presented a
method for incorporating many of these effects into the line shape model and performing an analysis of such spectra. Hopefully some of what was learned here can be applied to other studies. Such an approach could be particularly useful for measuring line mixing effects in molecules for which there is little or no knowledge about the relaxation matrix. A pertinent example would be methane (Pine, 1997b).

In terms of answering questions about the inclusion of CO$_2$ line mixing effects into an atmospheric model, we can make several comments. The EPG law does do a respectable job at capturing both the first and second order behaviour of line mixing. The observed residual using a second order model was on the order of 1% and using a higher order model was actually observed to increase the size of the residuals. Our measurements of mixing coefficients and line strengths suggest that, for any particular band, a more accurate description of line mixing might be obtained by direct measurement of mixing coefficients. These coefficients could then be used for a parametrised line shape model. For many CO$_2$ bands of interest this would require using a modified experimental setup so that measurements could be performed at 15μm.
CHAPTER 9

SUGGESTIONS and FUTURE WORK

As mentioned at the end of the last chapter, we have presented an experimental and analytic method which could be applied to study line mixing under other conditions or for other molecules. Here we give a brief outline for extensions of this work to investigate the present and other systems.

With the results of this thesis in mind we can re-evaluate the methods of analysis used for the first order line mixing results discussed in the previous chapter. The observation of intensity transfer at pressures below 10kPa is contrary to the earlier analysis of the medium pressure spectra under the Rosenkranz first order assumptions. It would appear that a more general analysis of the medium pressure spectra would show evidence of higher order line mixing effects. As previously mentioned the inclusion of higher order line mixing effects may change the line mixing measurements such that the sum law is satisfied. Analysis of the medium pressure spectra with the inclusion of higher order line mixing effects requires taking more spectra with the current experimental configuration which produces spectra with extremely flat baselines and without air contamination. Such medium pressure spectra may be fit for individual line strengths in addition to the other parameters already fit for in this thesis.

The most direct extension of this work would be to make similar measurements at other
temperatures, particularly low temperatures. Such work is completely possible and only requires the addition of a cooled, temperature controlled cell. The temperature dependence of both the broadening coefficients and the mixing coefficients are of interest and there has been very little experimental investigation of the temperature dependence of either parameter. A parametrised model of the line mixing temperature dependence has been published by Strow et al. (1994) and would be an interesting point of comparison. The applicability of the EPG law at other temperatures could be checked and the temperature dependence of the $\beta$ parameter examined.

Another extension is to look at the collapse of the $Q$-branch at higher pressures. The EPG law predicts that the $Q$-branch studied will show rapid collapse at pressures between 5 and 20 atmospheres. At these pressures the interbranch mixing that was ignored in this thesis will need to be considered. The experiments at these pressures would be better performed by a Fourier transform spectrometer since less frequency resolution would be required and the spectral range of a scan would need to be much larger than the 1.3 cm$^{-1}$ of our instrument.

Measurements in other buffer gases would also be possible. Such experiments would be best performed with weak mixtures of CO$_2$ so that self-broadening and self-mixing would be small. Such experiments would require a much longer cell than the 1m cell used in these experiments to achieve the necessary absorption. A helium buffer gas would be of theoretical interest since detailed computer models exist which calculate the CO$_2$ line shape starting from an estimate of the CO$_2$:He interaction potential (Green, 1989). Because helium is such a light gas we expect that speed-dependent effects will be minimal. Hence, the fits should be possible using a speed-independent line shape such as the hard collision model. From the point of view of atmospheric applications, measurements in N$_2$ and O$_2$ perturbers would give numbers of more direct application to remote sounding.

Other systems of interest that experience line mixing effects could also be investigated. This
would be most beneficial for systems in which no gap law has been either found or verified to adequately calculate the line shape. A good example of such a system is the CH$_4$ multiplets investigated by Pine (1997b). These systems have only a few lines involved in the mixing and hence the relaxation matrix is smaller. As Pine points out, there exists the possibility of uniquely calculating the relaxation matrix from the first and second order mixing coefficients. Pine has measured the first order mixing coefficients but not the second order coefficients.

The double hard collision model developed in this thesis may be a simple profile that accounts for the gross effects of speed dependence. Such a simple profile may have application to remote sensing where computationally cheap models are required. Further investigation of this profile in other systems may verify its general applicability. Work has already progressed in the application of this model to CO in buffer gases.

Speed-dependent effects will be most pronounced for small active-to-perturber mass ratios. A light molecule such as CH$_4$ in a heavy perturber like Xe should display strong speed-dependent effects. Such a system might provide an opportunity to investigate the effects of speed dependence on the line mixing component. From our simple examination of such effects we might expect to see a deviation from the dispersion line shape.
APPENDIX I

NORMALISATION METHODS

The Ge beam splitter divides the generated infrared power into two paths: approximately 2/3's of the power passes through the splitter, through the gas cell and is focussed onto a detector which measures the transmission signal; the other 1/3 of the power is reflected by the splitter and is focussed directly onto a detector which measures the normalisation signal. The normalised signal, \( \tau \), is defined to be the transmission signal, \( T \), divided by the normalisation signal, \( N \), where we use the subscript \( i \) to emphasize the discrete nature of the sampling. Thus, ideally, \( \tau \) would be a direct measure of the transmission of the gas in the cell, ranging from a maximum of approximately \( 2 \) (for no absorption by the gas) to \( 0 \) (for complete absorption by the gas).

We normalised the transmission signal to correct for fluctuations in infrared power caused by changes in visible beam power and overlap within the LiIO\(_3\) crystal. Although the infrared power fluctuations also cause both the transmission and the normalisation signals to fluctuate, \( \tau \) should remain a constant determined solely by the beam splitter and the transmission of the gas. Hence, at a given frequency the normalised signal is ideally a constant \( \tau = \tau \).

We used an analog-to-digital converter to simultaneously sample both signals, \( T \) and \( N \) and from these measurements we calculated the normalised signal, \( \tau' \),

\[
\tau' = \frac{T'}{N'} .
\]

where the prime distinguishes a measured quantity. In a noiseless system we could unambiguously determine the normalised transmission by a single pair of transmission and normalisation measurements.
APPENDIX I - Normalisation Methods

\[ \tau' = \tau'_1 = \frac{T'_1}{N'_1}. \] (I.2)

Of course any real experimental system has sources of noise. In an effort to estimate \( \tau \) better than can be done by a single pair of measurements, we average together many measurements. This raises the question of how to average the measurements to best determine the actual value of \( \tau \). The two most obvious methods can be represented as follows:

\[ A) \quad \tau' = \frac{\langle T'_i \rangle}{\langle N'_i \rangle} \]

\[ B) \quad \tau' = \frac{T'_i}{N'_i} \]

where \( \langle \rangle \) represents an average over many samples and \( \tau' \) is an estimator of \( \tau \). We will show here that the two methods can lead to systematically different estimates of \( \tau \).

The errors in \( T'_i \) and \( N'_i \) can be divided into correlated and uncorrelated errors. Correlation between \( T'_i \) and \( N'_i \) can only occur from two sources: fluctuations in the infrared power before being split and variations in the reflectivity of the beam splitter. Fluctuations in the infrared input power are expected and are the entire reason for performing the normalisation in the first place. Such variations are completely correlated in the transmission and normalisation signals and ratio to a constant, \( \tau \). These fluctuations can therefore not be considered error sources. The only other source of correlation between the two signals is the variation in \( \tau \), resulting from the spatial and frequency dependencies of the beam splitter. For the purposes of this argument we will assume such variations will contribute a negligible amount of error and therefore \( \tau = \tau'_i \).

All other sources of error: detector noise, analog-to-digital conversion error, and variations in gas transmission (due either to spatial inhomogeneity of the gas or frequency fluctuations in the
APPENDIX I - Normalisation Methods

infrared radiation), lead to uncorrelated errors in $T_i'$ and $N_i'$. We can represent the errors from these sources as $\Delta T_i$ and $\Delta N_i$ such that: $T_i = T_i' + \Delta T_i'$ and $N_i = N_i' + \Delta N_i'$.

Since $T_i$ and $N_i$ are considered to be the true signals without error and $\tau_i$ is assumed to be constant, we can write:

$$\tau = \frac{T_i}{N_i} = \frac{T_i' + \Delta T_i'}{N_i' + \Delta N_i'},$$

where we have replaced the true signals with the measured signals and associated errors. Rearranging this equation and taking the expectation of both sides, one gets,

$$\langle \tau(N_i' + \Delta N_i') \rangle = \langle T_i' + \Delta T_i' \rangle. \quad (I.5)$$

But $\tau$ is just a constant and can be taken outside the expectation operator. If we assume that the error distributions $\Delta T_i'$ and $\Delta N_i'$ are symmetric about zero, then their expectations are zero; hence after rearranging,

$$\tau' = \frac{\langle T_i' \rangle}{\langle N_i' \rangle}. \quad (I.6)$$

Here again we have used $\tau'$ to emphasis that it would be determined from actual measurements. This implies that normalisation method $B$ would be the correct method to use under the above assumptions.

It is now interesting to investigate method $A$ under the same assumptions. We can expand the numerator of method $A$ in terms of the errors,

$$\tau' = \frac{\langle T_i' \rangle}{\langle N_i' \rangle} = \frac{T_i - \Delta T_i'}{N_i'}. \quad (I.7)$$

But from equation I.4, $T_i = \tau N_i$, or substituting measured quantities,
Because $\Delta T'_i$ is not correlated to $N'_i$, the last term in the above equation is zero. However, $N'_i$ and $\Delta N'_i$ are correlated because $N'_i = N'_i + \Delta N'_i$. Therefore if we assume the error to be relatively small and use the first order binomial approximation for the denominator,

$$
\tau' = \left( \frac{\tau (N'_i + \Delta N'_i + \Delta T'_i)}{N'_i} \right)
$$

(I.8)

The first order term averages to zero but the second order term does not. Furthermore, since $\Delta N'_i$ and $N'_i$ are uncorrelated, the averages of the numerator and denominator can be separated,

$$
\tau' = \tau \left( 1 + \frac{\Delta N'_i}{N'_i + \Delta N'_i} \right) \approx \tau \left( 1 + \frac{\Delta N'_i}{N'_i} + \frac{\Delta N'_i^2}{N'_i^2} \right)
$$

(I.9)

The first order term averages to zero but the second order term does not. Furthermore, since $\Delta N'_i$ and $N'_i$ are uncorrelated, the averages of the numerator and denominator can be separated,

$$
\tau' = \tau \left( 1 + \frac{\sigma_N^2}{\langle N'_i^2 \rangle} \right)
$$

(I.10)

where $\sigma_N = \langle (\Delta N'_i)^2 \rangle^{0.5}$ is the standard deviation in the normalisation signal. The implication of these calculations is that method $A$ overestimates the normalised signal whereas method $B$ does not. For a signal-to-noise ratio of approximately 100, method $A$ overestimates the normalised signal by only $10^{-4}$.

It is important note that this result is dependent on the assumptions made about the sources and distributions of noise in the transmission and normalisation signals. More importantly this result suggests that methods $A$ and $B$ differ only by a constant offset. All evidence suggests that this offset was negligible for all the data shown in this thesis.
APPENDIX II

RESULTS

Pure CO$_2$ spectra are listed below in chronological order. All spectra were taken at 301°K.

Major changes to the system are noted below.

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## APPENDIX II - Spectral Files

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BIBLIOGRAPHY

Ph. Arcas, E. Arie, A. Valentin, and A. Henry, 1982: "Intensity of CO_2 Bands in the 4.8- to 5.3-μm Region. The (11'0,03'0)-00°0 Band", Journal of Molecular Spectroscopy, 96, 288-293.


L. Bonamy, J. Bonamy, S. Temkin, D. Robert, J.M. Hartmann, 1993: "State-to-State Rotational Cross-sections in Vibrational Modes - Application to the Infrared Q-Branch Profile for the (11'0)-00°0_1^13CO_2 Bending Band, J.
Bibliography


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Bibliography


D. P. Edwards, 1997: Personal communication.


F. Rachet, M. Margottin-Maclou, A. Henry, and A. Valentin, 1996: "Q-Branch Line Mixing Effects in the \((20^00)\leftarrow01^00\) and \((12^00)\leftarrow01^00\) Bands of Pure Nitrous Oxide Perturbed by \( N_2 \), \( O_3 \), and \( Ar \) and in the \( 13^00\leftarrow00^00 \) and \( 13^00\leftarrow01^00 \) Bands of Pure Nitrous Oxide", *Journal of Molecular Spectroscopy*, 175, 315-326.


Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
in D, determined from the Raman Q Branch, Physical Review A, 48, 3030-3035.


Philip L. Varghese and Ronald K. Hanson, 1984: "Collisional narrowing effects on the spectral line shapes measured at high resolution", Applied Optics, 23, 2376-2385.
