Photodissociation of Methyl Bromide
Adsorbed on LiF(001), NaCl(001), and MgO(001)

by

Darrick Vaughn Heyd

A thesis submitted in conformity with the requirements
for the degree of Doctor of Philosophy,
Graduate Department of Chemistry, in the
University of Toronto

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Thesis Abstract

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The adsorption and 193-nm photodynamics of CH$_3$Br adsorbed on LiF(001), NaCl(001), and MgO(001) have been studied by temperature programmed desorption (TPD) and angularly resolved time-of-flight mass spectrometry (TOF-MS), from submonolayer to multilayer coverages.

Both the translational energy distributions, $P(E_T')$, and angular distributions, $P(\Theta')$, of the CH$_3$ photofragments showed evidence of two pathways for CH$_3$ formation: direct (DIR) and indirect (IND). The DIR CH$_3$ was characterised by a gas phase-like $P(E_T')$ [van Veen et al., Chem. Phys. 92, 59 (1985)], with a high mean translational energy ($<E_T'\rangle$ = 2.3-2.4 eV) and a narrow width (FWHM = 0.6 eV), indicating that DIR CH$_3$ left the surface without collisions. The peak in the DIR $P(\Theta')$ gave the angle at which the Br-C axes of the molecules were aligned with respect to the surface normal prior to photolysis. For CH$_3$Br/LiF(001) the peak of the DIR $P(\Theta')$ showed that the Br-C axes were tilted approx. 20° from the surface normal. In the case of LiF(001) the DIR pathway predominated at high coverage (DIR/IND = 5.0 at 13.3 ML), but was a minor channel at low coverage. This was attributed to a gradual reordering of the adsorbate, in accord with results of polarised Fourier transform infrared spectroscopy (FTIR). The DIR $P(\Theta')$ of CH$_3$Br/NaCl(001) was
peaked at 38° irrespective of coverage, while for MgO(001) it was peaked at ~40° at submonolayer coverage and 22° at coverages >1 ML, indicating a change in orientation of CH₃Br/MgO(001). The DIR was a minor channel on both NaCl and MgO at all coverages (DIR/IND≤0.2), suggesting that CH₃Br(ad) primarily lay down on these substrates with the Br-C axis near the surface plane, an inference also in accord with FTIR results.

The IND methyl photofragments had markedly lower <Eₜ'> than DIR, indicating that they had suffered collisions in leaving the surface. For LiF(001), only a single peak at 1.0 eV was observed, while NaCl(001) and MgO(001) showed evidence of two IND channels, centred at 1.1 and 0.6 eV; these were termed IND(1) and IND(2). A striking finding was that the IND P(Eₜ') were of similar width to DIR, despite the strong collisions, suggesting constrained dynamics due to surface alignment. The two IND channels of MgO could be separated. The change in P(Θ') of the IND(1) channel of MgO with coverage mirrored the changes in the DIR P(Θ'), indicating that the Br-C bond direction was preserved in the IND P(Θ') dynamics as in DIR recoil. Similarly, on LiF the IND P(Θ') for multilayer coverages showed a modest rise near 20°, the peak in the DIR P(Θ'), indicating that some of the IND methyls retained the initial bond direction. Participation of the exchange reaction CH₃+BrCH₃'(ad) → CH₃Br + CH₃' was proposed to explain retention of the bond direction in the IND CH₃' for the single indirect channel of LiF and for IND(1) on MgO.
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Chapter 1. Introduction

1.1 A General Overview of Reaction Dynamics on Surfaces

The study of the photodynamics of adsorbed molecules on single-crystal surfaces has recently been an area of rapid growth.\textsuperscript{1-3} The motivation behind much of this work has been to control reaction dynamics by restricting the geometries of the reagent photofragments and their collision partners, both in the centre-of-mass and laboratory reference frames. Such control, which is not available in the gas phase, may result in altered reaction rates and modified branching ratios. These changes should be revealing of the potential energy surfaces (pes) governing reaction. Additionally, the changes in the photophysics of adsorbed molecules (modified pes) due to perturbations from the surface interactions are of interest.

Figure 1.1 shows schematically some of the photoprocesses which have been observed for adsorbates stimulated by uv irradiation. (The location of photon absorption is indicated by asterixes.) Panel 1.1(a) shows two processes involving photofragmentation of adsorbate molecules by direct absorption of the photon by the molecules: photodissociation (PDIS) and photoreaction (PRXN). Photodissociation is the first step in PRXN. Two examples of PRXN are shown: abstraction (ABST) and exchange (EXCH). Such 'adsorbate mediated' pathways are usually quenched by metallic and semiconductor substrates unless the adsorbate molecules are sufficiently removed from the surface.\textsuperscript{1} On insulator substrates, however, these processes are observed since the adsorbate-surface interaction, and therefore quenching, is weak. Panel
Figure 1.1: Photoprocesses of adsorbates. (a) Adsorbate excitation, fragmentation, and reaction. PDIS=photodissociation; PRXN=photoreaction; ABST=abstraction; EXCH=exchange. (b) Molecular desorption on insulators. PEJ=photoejection; PDES=photodesorption. (c) Photoprocesses on conductors. CT/PDIS=charge-transfer photodissociation; ESD=electron-stimulated desorption.
1.1(b) shows two pathways that lead to desorption of entire molecules from insulator surfaces: photoejection (PEJ), is adsorbate mediated, while in photodesorption (PDES) is substrate mediated. The last panel, 1.1(c), shows two electron-stimulated processes common to conducting surfaces: charge-transfer photodissociation (CT/PDIS) and electron-stimulated desorption (ESD).

The simplest adsorbate-mediated process is photodissociation (PDIS). In PDIS the molecule is promoted to a dissociative electronic state and ejects a radical fragment, usually with kinetic energies on the order of eV. This is exactly analogous to gas-phase photofragmentation, and has been found, on insulator substrates, to give similar photofragment kinetic energies and dissociation cross-sections to those found in the gas phase. If, however, the adsorbate geometry is such that the departing photofragment encounters a neighbouring molecule before being deflected from the surface, inelastic processes such as photoreaction (PRXN) may result. In fig. 1.1(a) two reactive pathways are shown: (1) abstraction (ABST) in which a departing photofragment collides with a neighbouring molecule with a large impact parameter, separating a fragment from the molecule and thereby forming a new product, and (2) exchange (EXCH) in which the departing photofragment attacks the neighbouring molecule with a low impact parameter, again forming a new molecule but ejecting a secondary fragment along the continuation of the direction of approach.

Photoejection (PEJ) and photodesorption (PDES) both lead to molecular desorption from the surface. Photoejection involves absorption of light by an adsorbate molecule. The excited molecule (M*) is able to form a bound complex
with a neighbour (M), which causes the two molecules in the complex to move towards each other. After quenching of the electronic excitation the complex, M*M, drops onto the repulsive part of the ground-state potential, which results in an impulse along the M*-M direction. In contrast, PDES involves absorption of light by surface defects or contaminant atoms, which results in a distortion of the substrate lattice. The resulting shock wave ejects the adsorbate molecules. Translational energy distributions from PEJ are non-Boltzmann, with \( <E_T'> \approx 0.1 \text{ eV} \). Photodesorption tends to yield lower mean translational energies (\( <E_T'> \approx 0.01 \text{ eV} \)) and distributions which can often be described as Boltzmann.

Photoelectron-stimulated processes, often grouped under the heading of desorption induced by electronic transitions (DIET), are important on metals and semiconductors, which have smaller band gaps and work functions than insulators. Because metal substrates are beyond the scope of this study, the reader is referred to some recent papers and reviews for further background.\(^1,3,4\)

Two important photoelectron-stimulated processes are charge-transfer photodissociation (CT/PDIS) and electron-stimulated desorption (ESD). The former is related to dissociative electron attachment and what is termed the 'harpooning' mechanism in the gas phase.

Photoelectrons from the metal substrate are transferred to an affinity state of the adsorbed molecule, forming an unstable anion which promptly dissociates. Usually CT/PDIS will dominate PDIS in the first monolayer on a metal. It has been found that CT/PDIS greatly increases the cross-section for photodissociation at the red end of the spectrum. The process of CT/PDIS has been studied by observing the ejected anionic fragments directly.\(^5\) These
fragments are energetic enough to undergo reactions. Evidence of the bimolecular nucleophilic substitution reaction $\text{Cl}^- + \text{CH}_3\text{Br} \rightarrow \text{ClCH}_3 + \text{Br}^-$ on Ag(111) has been reported. In ESD a photoelectron attaches to the adsorbed molecule, forming an anion which is attracted to the surface by its image charge. When the electron is transferred back to the substrate the neutral molecule finds itself too close to the surface and is repelled.

Because photoelectrons are produced with a wide range of energies (owing to the dispersion in the electronic bands of metals and semiconductors) CT/PDIS forms photofragments with a wide range of kinetic energies. By contrast, PDIS involves the absorption of a very well-defined energy determined by the laser wavelength, and so produces fragments with a narrow distribution of translational energies. The narrow $P(E_T)$ available from PDIS, as opposed to CT/PDIS, makes PDIS attractive for reaction dynamics studies. Insulators, with their low efficiency for quenching of PDIS, and small perturbations of the electronic states of adsorbed molecules, are ideal for studying the effects of alignment on reaction dynamics.

1.2 A Review of Some Recent Literature

A number of photochemical studies of adsorbates on insulators have been performed to date. These have been conducted primarily on alkali halides and insulating oxides. In this laboratory CH$_3$Br,$^7$-10 H$_2$S,$^7$,$^11$ OCS,$^{12}$-15 C$_2$H$_3$Cl,$^{16}$ HBr,$^{17}$ NO$_2$,$^{18}$ HI,$^{19}$ and (NO)$_2$$^{20}$ adsorbed on LiF(001) have been studied by excimer irradiation and time-of-flight mass spectrometry (TOFMS). Theoretical calculations have been performed in this lab. on the orientation.
localised atomic scattering (LAS) and PRXN of HBr\textsuperscript{21-24} and HI\textsuperscript{19} adsorbed on LiF(001). Photolysis of methyl bromide adsorbed on LiF(001) has also been studied by Tabares et al.\textsuperscript{25} (Details of experiments performed on CH\textsubscript{3}Br in the gas and adsorbed states are presented in sections 1.3 and 1.4.) The photolysis of CH\textsubscript{3}I and CD\textsubscript{3}I adsorbed on MgO has been investigated by resonantly-enhanced multiphoton ionisation (REMPI) and TOFMS.\textsuperscript{26-29} and by theory.\textsuperscript{26,30} Photolysis of ClNO on rough MgO and on single-crystal MgO(001) has also been studied by REMPI and TOFMS.\textsuperscript{31,32} Photodissociation of ICl and IBr on MgO(001) have been examined theoretically by McCarthy et al.\textsuperscript{33,34}

The phenomenon most frequently observed in the photolysis of adsorbates on insulators is PDIS; it has been reported for all the studies listed above. As previously mentioned, PDIS on insulators is somewhat analogous to gas-phase photolysis; nonetheless, the surfaces can have a substantial influence on the dynamics. In the case of OCS, for example, an increase in the cross-section by 3-4 orders of magnitude was observed.\textsuperscript{12,15} This was ascribed to electronic energy transfer from crystal defects. Additionally, translational energy distributions (P(E\textsubscript{T}')) of photofragments can be modified from those of the gas phase. For OCS/LiF(001) the S fragments were much more energetic than their gas phase counterparts. This implied a dramatic decrease in the branching ratio of spin-orbit excited S\textsuperscript{*} to ground state S, as well as a decrease in the rotational excitation. The methyl P(E\textsubscript{T}') from PDIS of CH\textsubscript{3}Br/LiF(001) in the early work from this lab.\textsuperscript{9} was found to be sensitive to coverage and was different for annealed and unannealed LiF(001). Bromine fragments were observed in the TOF with higher energies than those of the gas phase. This was ascribed to 'chattering': collisions in which the CH\textsubscript{3} fragments recoiling from the LiF surface had multiple encounters with the more slowly recoiling Br
atoms. Slight perturbations in the electronic states of C₂H₃Cl, due to the presence of a LiF(001) surface resulted in two pathways for PDIS to produce Cl* and Cl in two electronic states, rather than the one seen in the gas phase.¹⁶

Surface-aligned photoreactions (PRXN) have been reported for many of the systems mentioned above. Abstraction (ABST) has been observed for H₂S,¹¹ OCS,¹³ and HBr¹⁷ on LiF(001); the products were H₂, S₂, and H₂. Theory has predicted that exchange (EXCH), producing H atoms, should also be a major pathway for HBr.²⁴ Bimolecular photoreaction (PRXN(B)) has been reported for HBr/LiF.¹⁷ This involves excitation of an HBr dimer and subsequent formation of H₂+Br₂, without direct photolysis of HBr. The same bimolecular process has been observed for HCl/LiF(001). Abstraction was also found to produce HCl in C₂H₃Cl,¹⁶ in contrast with the gas phase for which the only direct pathway to HCl was via elimination.

Photoejection (PEJ) has been observed for H₂S,¹¹ OCS,¹⁴ C₂H₃Cl¹⁶ and CH₃Br¹⁰,²⁵ on LiF(001). The primary difference between PEJ and photodesorption (PDES), as mentioned in section 1.1, is that PEJ involves excitation of the adsorbate, whereas in PDES the substrate is the absorbing species. Because pure LiF is transparent to uv light (the band gap is 14 eV), PDES can only occur for impure, or defective, crystals. Hence, it is very dependent on crystal preparation, and is often not observed. PEJ translational energy distributions are non-thermal. The yield of PEJ is found to increase dramatically with coverage between the first and second layer, indicating that the underlayer ejects the overlayer. Correspondingly, photoejection of CH₃Cl from double layers of CH₃Cl(1 ML)/CH₃Br(1 ML)/LiF(001) and CH₃Br(1 ML)/CH₃Cl(1 ML)/LiF(001) showed that the PEJ
yield was dependent on the absorption cross-section of the lower layer, and that the ejected molecule came from the top layer.\textsuperscript{10}

1.3 Photodissociation of CH$_3$Br in the Gas Phase

Gas-phase studies of CH$_3$Br photodissociation have been performed by van Veen et al.\textsuperscript{36} The experiments were performed on a pulsed molecular beam of CH$_3$Br at photolysis wavelengths of 193 and 222 nm. The A band of CH$_3$Br is known to have three components which are denoted $^1Q$, $^3Q_0$ and $^3Q_1$ (see fig. 1.2(a)). At 193 nm the states accessed are the $^1Q$ and $^3Q_0$, via perpendicular and parallel transitions respectively. The $^1Q$ state correlates to the ground state Br($^2P_{3/2}$) + CH$_3$. while the $^3Q_0$ state correlates to excited Br*(2P$_{1/2}$) + CH$_3$ (the spin-orbit excitation energy, $E(\text{Br}^*)-E(\text{Br})=0.456$ eV). Photodissociation from all of the Q branches is direct with a quantum efficiency of 1. Anisotropy parameters derived from angular distributions of the CH$_3$ photofragments indicated that the ratio of Br:Br* was 4:1 at 193 nm. Adiabatic crossing between the exit channels was found to be unimportant ($\leq$6\%) in CH$_3$Br(g). The C-Br bond dissociation energy was determined as 2.87\pm 0.02 eV from the maximum energy in the CH$_3$ time-of-flight. The cross-section for photodissociation is 4.5\times 10^{-19} cm$^2$ at 193 nm.

Because the CH$_3$ is ejected quickly from the CH$_3$Br molecule, it is formed initially with the (strained) C$_3v$ geometry of the parent molecule, rather than the D$_{3h}$ symmetry of the free radical. It therefore exhibits vibrational excitation in the $v_2$ (umbrella mode). (Since the impulse is directed along the C-Br axis, it is unlikely that any other modes would be excited.) By fitting
Figure 1.2: (a) Schematic diagram of the ground electronic state (X) and excited electronic states (Ω manifold) of CH₃Br(g). The ¹Ω and ³Ω₀ states are accessed with 193 nm radiation. (b) Energy distribution of CH₃ photofragments from 193 nm photolysis of CH₃Br(g). Horizontal arrow indicates FWHM. After van Veen et al.³⁶
the time-of-flight envelope, van Veen et al. estimated that the ejected CH3 had an internal energy distribution peaked at ca. 2-3 quanta in the v2 mode and extending out to ~9 quanta. The internal excitation, superimposed on the energies of the exit channels (Br and Br*) results in a translational energy distribution of the CH3 photofragments from the collision-free gas-phase photodissociation whose centre is at 2.5 eV and whose full width at half maximum is 0.5 eV (fig. 1.2(b)).

1.4 Photochemistry of CH3Br on Surfaces

The photochemistry of CH3Br on metal surfaces has been studied extensively. As this study deals with insulator substrates only, the reader is referred to the works from the research groups of J.M. White, A.M. Bradshaw, and Harrison. (The review by Zhou, Zhu, and White contains many pre-1991 references.) The structure and CT/PDIS dynamics of CH3Br adsorbed on GaAs(110) (a semiconductor) was studied by R.M. Osgoode, Jr. and co-workers.

The first studies of the photochemistry of CH3Br adsorbed on insulator substrates were conducted in this laboratory by Bourdon et al. and by Harrison et al. using LiF(001) as substrate. These were followed by the work of Tabares et al. on the same surface. Recently, a series of three studies of the photodynamics of CH3Br adsorbed on LiF(001) and NaCl(001), and on MgO(001) was completed in this laboratory. In addition to these experiments two theoretical simulations have appeared on the photodissociation and structure of CH3Br/LiF(001).
The first studies of the photodynamics of CH$_3$Br/LiF(001) were conducted in this laboratory at a photolysis wavelength of 222 nm and a surface temperature of 117 K, a temperature at which, at $\geq 0.2$ ML coverage, the desorption rate is very high. The crystals used in these studies also showed a high yield of photodesorption, probably due to impurity atoms in the crystals. Methyl bromide coverage was kept at steady state in these experiments by backfilling the chamber at a constant pressure of CH$_3$Br while the time-of-flight measurements were being taken. Such 'continuous dosing' was advantageous when several thousand laser pulses were needed to collect a single spectrum.

Under these conditions, the angular distributions of CH$_3$ photofragments indicated that the figure axes of the molecules were directed along the surface normal. Translational energy distributions of CH$_3$ indicated that many of the methyls escaped without collisions, suggesting that the molecules that produced them must also have been oriented with the CH$_3$ group pointing away from the surface. Bromine photofragment translational-energy distributions showed a high-energy tail, with energies greater than those obtained from the gas phase. It was concluded that some of the molecules had Br directed away from the surface, so that the high-energy tail could be caused by methyl radicals recoiling from the surface and striking the slow-moving Br atom in multiple collisions. This mechanism, termed 'chattering,' was confirmed by the classical trajectory simulations of Huang and Guo$^{49}$ and of Watson et al.$^{48}$ It was concluded from those studies that CH$_3$Br was oriented along the surface normal, with molecular dipoles alternately pointing towards and away from the surface.
Temperature programmed desorption (TPD) performed in those studies indicated that the desorption energy decreased as the coverage increased in the submonolayer range. This led to the conclusion that at low coverage intermolecular repulsions were strong. It was thought that those repulsions would probably be sufficient to keep the molecules separated, so that they would 'wet' the surface.

Experiments performed by Tabares et al. on the same system at 193 nm and a surface temperature of 30 K led to quite different results. In these experiments CH$_3$Br was dosed from a pulsed nozzle before, and not during, laser irradiation. Both translational-energy distributions and angular distributions suggested that the greater part of the photofragments had escaped following collisions, and therefore the molecular axes of the CH$_3$Br molecules could not have been directed along the surface normal. Additionally, the TPD spectra obtained in this study showed a single desorption energy at all coverages, suggesting that adsorbate-substrate and adsorbate-adsorbate interactions were similar. Wetting probably did not occur on this surface, since at this temperature it was improbable that adsorbate molecules would migrate to the substrate. Instead, three-dimensional islanding and a disordered structure was proposed.

It is likely that the differences in the results of the studies from this laboratory and those of Tabares et al. were due to the different surface temperatures used in the two studies. At the low temperature used in the Tabares et al. study, the molecules were probably not very mobile, hence they did not achieve the favourable geometry observed in the studies conducted at 117 K. This explanation is plausible in light of the helium atom scattering
studies of Robinson et al. The helium diffraction data from CH₃Br/LiF(001) was consistent with the ordered, anti-feral structure proposed to explain the results from the earlier photodissociation studies. However, the structure could only be obtained by annealing the surface as the CH₃Br was dosed. Lower dosing temperatures tended to produce disorder.

Molecular simulations of CH₃Br adsorption and photodissociation have been performed on both smooth and defect-laden LiF(001) by Watson et al. as well as on smooth LiF(001) by Huang and Guo. Watson and co-workers computed the minimum-energy adsorption geometry with the Br atom over a Li⁺ and the CH₃ over a neighbouring F⁻. The methyl group was tilted slightly upward from the surface plane at an angle of 73° from the surface normal. Those findings paralleled those obtained by both theory and polarised fourier-transform infrared spectroscopy in this laboratory for the preferred adsorption of HBr on the same substrate. They will be confirmed for CH₃Br/LiF(001) by an FTIR study performed in conjunction with the present work. In addition, Watson et al. simulated photodissociation dynamics from the three low-order faces of the b-phase CH₃Br crystal--the a, b, and c faces. Molecules in the b face lie parallel to the surface. In the a and c faces, the molecules are angled respectively 65° and 25° from the surface normal. Watson et al. found that for well-ordered surfaces the energy distributions of photofragments escaping without collisions were similar to those found in the gas phase. Collisions tended to reduce the mean energy of the CH₃ photofragments. Watson et al. also showed that for CH₃Br with the CH₃ oriented towards the surface 'chattering' between a CH₃ recoiling from the surface and the departing Br could increase the Br kinetic energy leading to a high energy tail, as seen in the energy distributions of Harrison et al. The angular distributions of non-colliding photofragments were found to peak at the
angle of tilt of the C-Br axis. Collisions broadened and obscured the peaks in the angular distributions.

In the work of Huang and Guo adsorption geometries were also calculated. The most stable structure from this study had two adsorption geometries: one with the methyl upward and the C-Br bond axis tilted 12±7° from the surface normal, the other with the CH₃ pointed downward and the molecules tilted 12±8°. This structure was in general agreement with the experimental results of Harrison et al.⁹ Photolysis wavelengths of 193 and 222 nm were used in this study. Results of the simulated photolysis from this surface were consistent with those of Harrison et al., with similar CH₃ energy distributions, angular distributions peaked near the surface normal. Huang and Guo, like Watson et al., also observed 'chattering' in their calculations, which increased the kinetic energy of the departing Br atoms up to 1 eV with a single collision.

1.5 Summary and Thesis Preview

Adsorbing molecules on single-crystal substrates provides a means of controlling reaction dynamics. Because the molecules adsorb with specific geometries, the departing photofragments collide with neighbouring molecules with a restricted range of impact parameters. The photochemistry of adsorbed molecules is performed on insulators substrates because these surfaces cause only small distortions of the adsorbate energy levels, and have poor electronic quenching efficiencies and large band gaps, thus eliminating charge-transfer processes. The electronic transitions of molecules adsorbed on insulators tend.
therefore, to be similar to the gas phase. The changes in dynamics are therefore largely attributable to surface alignment. While many studies of the photochemistry of adsorbed CH$_3$Br have been performed on conducting substrates, fewer have been done on insulators. Almost totally lacking are comparative studies of adsorbate photochemistry for a single adsorbate on a series of chemically-related substrates.

In this thesis the results of photochemistry studies of CH$_3$Br adsorbed on three ionic insulator substrates are reported. The substrates chosen were LiF(001), NaCl(001), and MgO(001). All three substrates have electronic band gaps greater than the photon energy (LiF, 13.7 eV; NaCl, 8.8 eV; MgO, 7.8 eV$^{52}$), and all share the sodium chloride structure. The (001) plane is a square net. The unit mesh parameters for this plane are: LiF, 2.96 Å; NaCl, 4.00 Å; MgO, 3.00 Å.$^{53}$ It will be demonstrated in this thesis that the difference in the unit mesh sizes of LiF and NaCl results in a large change in the adsorbate structure of CH$_3$Br(ad). Although MgO(001) resembles LiF in its mesh size, it differs by a factor of two in the coulombic attraction to the substrate atoms.

Marked differences in the energy distributions and angular distributions of the photofragments were observed for these three systems. In Chapter 2 the experimental techniques are discussed, including details of the time-of-flight mass spectrometer and an overview of temperature programmed desorption analysis. Chapters 3, 4, and 5 present the results of studies performed on LiF(001), NaCl(001), and MgO(001), respectively. Primarily, the results concern the angular and energy distributions of CH$_3$ photofragments from photodissociation. These dynamical properties (as noted above) depend mainly on the adsorbate structure. Structures that are consistent with the data will
be proposed. Temperature programmed desorption profiles will also be presented. These show major differences for adsorption on the three surfaces. In chapters 3 and 5, evidence for involvement of a new reaction pathway, termed *exchange*, is presented.
Chapter 2. Experimental

2.1 Experimental Apparatus

Ultra-high Vacuum Chamber

Experiments were performed in an ultra-high vacuum (UHV) chamber (fig. 2.1) fitted with an Extrel quadrupole mass spectrometer (QMS) and a Perkin-Elmer low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) system. Surface characterisation of insulator substrates with AES was not feasible due to surface charging which lowered the intensity of the peaks, and also accumulation of defects on the substrate surfaces observable in temperature program desorption experiments. Damage of NaCl(001) by electron irradiation has been reported previously.\textsuperscript{54,55}

UHV conditions were necessary to ensure that the surface under study remained uncontaminated by background gas molecules. According to simple collision theory, the number of molecules impinging on a surface per unit area per unit time is

\[
N = \frac{p}{\sqrt{2\pi m k T}}
\]

where \( p \) is the pressure of gas in the chamber, \( m \) is the mass of the gas molecules, \( k \) is the Boltzmann constant, and \( T \) is the absolute temperature.\textsuperscript{19} For \( p=10^{-10} \) torr, \( m=18 \) amu (H\(_2\)O), and \( T=300 \) K, \( N=5\times10^{10} \) collisions\( \cdot \)cm\(^{-2} \cdot \)s\(^{-1} \). Assuming a typical value of \( 5\times10^{14} \) adsorption sites per cm\(^2 \), such a collision rate would result in 10% contamination of the surface in about 15 minutes, assuming every impinging molecule stuck to the surface. For this system, 15
minutes was ample time to perform an experiment. The surface was flash heated between experiments to remove contaminants. The major gas-phase contaminants, according to the mass spectrum, were H₂, CO₂, and H₂O, in descending order.

The main chamber (fig. 2.1), which contained the sample, was pumped by a Balzers TPU 170 (170 L•s⁻¹) turbo-molecular pump, backed by an Edwards model E02 diffusion pump whose exhaust was pumped by an Edwards model E2M8 two-stage mechanical pump. A base pressure of <1×10⁻¹⁰ torr was attained in the main chamber after bake-out. The chamber had to be heated (baked) to about 100°C to remove adsorbed water from the walls.

The QMS chamber was connected to the main chamber by way of two 0.32-cm diameter apertures located at the entrance and 13.0 cm from the entrance of the ioniser region of the QMS. The volume between the two apertures was pumped by a 20 L•s⁻¹ Perkin-Elmer ion pump, while the volume containing the QMS was pumped by a combination of a 60 L•s⁻¹ Perkin-Elmer ion pump, a titanium sublimation pump, and a cryotrap cooled by liquid nitrogen. Differentially pumping the QMS chamber minimised the background signal during experiments.

**Quadrupole Mass Spectrometer**

An Extrel quadrupole mass spectrometer (QMS) was used both for temperature-program desorption and time-of-flight experiments. The QMS consisted of an axial ioniser (model 041-1) mounted atop a quadrupole filter. The distance between the centre of the sample and the ioniser (i.e. the flight path) was 23.6 cm. The axes of the ioniser and quadrupole filter were in line-
of-sight of the two 0.32-cm apertures. (Henceforth, the line of sight defined by the two apertures will be called the detection direction.) In addition to allowing for differential pumping of the QMS chamber, the 0.32-cm apertures served as defining elements, reducing the field of view 'seen' by the QMS to a disk 9 mm in diameter on the crystal and ensuring that the molecules and fragments detected by the QMS originated from the sample and not, for example, from the sample mount or the chamber walls over the full range of viewing angles. The apertures also limited the angular acceptance of the QMS to 3°, which allowed angularly-resolved measurements to be made.

The voltages on the ioniser optics were regulated by a model 020-2 ioniser control unit. Typical settings for the unit were: electron energy, 70 V; emission, 20 mA; ion energy, 50 V; extractor, 40 V. Lenses 1, 2, and 3 were adjusted for maximum transmittance and best peak shape. It was found convenient to adjust the ion optics while observing the water peaks (16, 17, and 18 amu) in the sweep mode. When properly adjusted the intensities of the signals from the water peaks should ascend in the order $I_{16} < I_{17} < I_{18}$. Splitting of the peaks was sometimes observed due to the high value of the ion energy. Because of the sharpness of the split peaks, the measurements were sensitive to quadrupole drift; however, that problem was easily overcome by tuning to the exact peak of the mass signal before each measurement was taken. While peak shape could be improved by lowering the value of the ion energy, a recalibration of the time for an ion to travel the length of the quadrupole ($t_{quad}$) was necessary. For lower ion energies it was also necessary to take account of the kinetic energy of the newborn photofragments when calculating $t_{quad}$. 
A model 011-1 quadrupole power supply was used to control the filter. It consisted of three components: the quadrupole control, the radio frequency power source, and the high-Q head. The radio frequency power source produces a tunable, oscillating signal (1-6 MHz) which is fed into the high-Q head. The high-Q head steps up the signal from the oscillating power source to a level capable of driving the quadrupole filter. The circuit is controlled and monitored by the operator by means of the quadrupole control unit. Two high-Q heads were used: the model 12, with a range of 0-80 amu, and the model 15, range 0-400 amu. Because of the former's superior sensitivity and resolution (<1 amu) at low masses, it was used almost exclusively except when higher mass range was necessary.

A conversion dynode and channeltron mounted off-axis (i.e. out of the detection direction) comprised the detection system. The conversion dynode was biased at -3.5 kV, and the front of the channeltron at -2.2 kV, to provide maximum gain (~107). Signals from the channeltron were conducted through a BNC feedthrough to an amplifier outside the chamber.

**Detection Electronics**

The detection electronics for the time-of-flight experiments have been described elsewhere. The signal from the QMS was amplified 100x (Philips 6093) and then sent to a pulse discriminator (PRA 1762). The pulses from the discriminator were counted by a LeCroy 3521A multichannel scaler (MCS), using a bin width of 1 μs (the minimum bin width for the instrument). The MCS was mounted in a Camac crate (Kinetic Systems model 1500) and interfaced with the computer (Apple Macintosh SE/30) via a LeCroy 6010 "Magic Controller" equipped with a general purpose interface bus (GPIB). The
output of the MCS (counts) was stored in a memory module (LeCroy MM8201A), also mounted in the Camac crate. With each laser pulse 1024 1-μs bins were stored in the memory module. After 16 laser pulses the module was read and reset by the computer.

The laser pulse and collection electronics were all synchronised with a home-built MCS controller. The purpose of the controller was to provide a stable 1.000 MHz square-wave clock to advance the MCS to the next bin, as well as to provide triggers for the laser that were synchronised to the clock. Data collection began with a pulse that was sent from the the computer, via the Magic Controller, to the home-built MCS controller. The MCS controller would then send the first of two triggers, via a pulse shaper (also homebuilt), to the laser; this first trigger was synchronised with the clock and started the laser’s capacitor charging for the next shot. A second trigger, also synchronised with the clock, was sent 10.0-10.8 ms after the first (the delay could be set by the user) to both the laser and the MCS. The effect of the second pulse was to cause the laser to fire and the data collection to begin. While the laser could be operated with one control pulse, synchronisation with the start of data collection had to be better than 1 μs, necessitating the second pulse. In addition, better power stability (± 5% shot-to-shot) could be obtained with two triggers. The laser was found to discharge spontaneously with delay between triggers of >10.8 ms. Both the laser pulse and data collection began simultaneously, as evidenced by a sharp spike in the time-of-flight spectrum at zero time, due to pickup of the laser discharge by the preamplifier.
**Laser**

Methyl bromide was photolysed using a Lumonics excimer laser (model TE-860-3) with an Ar-F₂ fill (193 nm). The laser beam was apertured to 8 mm dia. with an iris and reflected 90° with a dielectric mirror through a Suprasil window and onto the sample. The radiation transmitted by the dielectric mirror impinged on a joule meter (Molecron J3-05), the signal from which was amplified and measured by a home-built sample-and-hold circuit, digitised with an analogue-to-digital converter (Stanford SR245) and read by a Labview computer program while the time-of-flight spectrum was being collected. The signal from the sample-and-hold was converted to a laser fluence impinging on the sample by obtaining the ratio of the intensity of the reflected beam, measured with a laser power meter (Scientech 361), to the sample-and-hold signal due to the transmitted light.

**Sample Mount**

The sample mount was designed to provide rapid heating and efficient cooling (fig. 2.2). Cooling was achieved through a liquid-nitrogen-cooled beryllium-copper finger, which had a capacity of ~10 mL and was supplied with liquid N₂ through a 1/8" tube and vented with another. To the finger was attached a forked piece, termed a *yoke*. The yoke used for the LiF(001) and NaCl(001) work was made of oxygen-free high-conductivity (OFHC) copper, but because of the high temperatures needed to anneal and oxidise the MgO(001) sample, a molybdenum yoke was used for that work. The arms of the yoke were milled flat. Across the arms a Ta stage was fastened. For the LiF and NaCl work, the stage was bolted directly to the arms of the yoke, but for the MgO work the stage was separated from the arms by sapphire spacers (Edmund; 1 mm thick). While the two extra junctions between the sample and the cold
finger produced by the inclusion of the spacers decreased the cooling efficiency of the mount (base temperatures were typically 5-10 K higher with the spacers as without) the low thermal conductivity of warm sapphire allowed the sample to be heated to high temperatures without excessive heating of the yoke and cold finger.

The samples were attached by retaining clips (made of stainless steel for the LiF and NaCl work, and Ta foil for the MgO work) which were screwed to the tantalum stage with 2-56 stainless screws. Surface temperature was monitored by use of a chromel-alumel thermocouple (Omega) which was spot welded to the underside of one of the clips and sandwiched between the clip and the sample.

Efficient cooling (90-100 K) was achieved with liquid nitrogen. A 4-L dewar fed liquid N2 through the Be-Cu cold finger by gravity. The vent line on the finger was pumped by a vacuum pump (Gast 0523-V4-G180DX). This arrangement of gravity feeding and pumping was more efficient than the previous use of high pressure (50 psi) to push liquid N2 through the cooling lines. By pumping on the vent line, a further cooling of the liquid nitrogen is achieved thermodynamically, and the base temperatures achieved were found to be 10-15 K lower than was previously possible.

The samples were heated radiatively with a filament located behind the Ta stage. The filament was supplied by a floatable power supply (Kepco ATE 25-10M), which was equipped with an interface card for remote control. At maximum current (5 A) the filament dissipated approx. 120 W of power. Filaments were made by wrapping 0.25-mm tungsten-3% rhenium wire
**Figure 2.2:** The liquid nitrogen-cooled sample mount. Liquid nitrogen was gravity-fed into the reservoir and actively pumped out. A base temperature between 90-100 K could be attained with this design.
Johnson-Matthey 10073) about a rod of suitable thickness (~2 mm). A ceramic rod (Kimball Physics Al₂O₃) was sometimes inserted into the filament coil to ensure that the filament did not become distorted with heating and cooling.

The filament was shielded on 5 sides with Ta foil and on the sixth side by the Ta sample stage (see figs. 2.2 and 2.3). Further shielding was provided by Ta-foil "wings" which were spot welded to the stage (fig. 2.3). The shielding was necessary for electron-bombardment heating as it was found that electron bombardment with an unshielded filament caused defects that were observable as high-temperature peaks in the temperature program desorption. The defects could be removed by annealing. While no results reported in this thesis were obtained from electron-bombarded samples, the shielding was still used to ensure that any metal that may have evaporated from the filament did not contaminate the substrate surfaces.

The arms of the yoke were bent as in fig.2.2, 7° for LiF and NaCl, 4° for MgO, to allow the laser beam, which entered a window at the top of the chamber, to propagate along the rotation axis of the sample and to strike the crystal at glancing incidence. For angularly-resolved time-of-flight experiments this arrangement kept the angle of incidence, and therefore the polarisation, of the laser beam constant with rotation angle.

The entire sample mount assembly was mounted on a rotatable xyz manipulator. The xyz translators were used to position the sample in the centre of the chamber, so that the excimer laser spot always struck the crystal in the middle of the QMS field of view (as defined by the apertures).
**Figure 2.3:** Detail of sample stage, showing shielding of filament. The filament shield (side view) surrounded the filament on five sides, but only three could be shown in this view.
**Crystals and Gases**

The 10×10×20 mm³ substrate single crystals (LiF and NaCl from Solon; MgO from Marketech) were cleaved either with a razor blade and a tack hammer (LiF and NaCl), or a utility-knife blade and a claw hammer (MgO) to 1×10×20 mm³. All samples were cleaved under dry nitrogen. It has been reported that samples of NaCl(001) cleaved under dry nitrogen show similar adsorbate vibrational features, studied by Fourier transform infrared spectroscopy (FTIR), and diffraction patterns as those cleaved *in situ* under vacuum.

Samples of LiF were γ-irradiated at the factory for ease of cleaving; the defects produced by the irradiation (F-centres and M-centres) hardened the crystals and made them more brittle and easier to cleave. The defects also produced a yellow colour in the LiF, which in the non-irradiated form is colourless. The colour was removed by annealing.

All samples were cleaned and prepared before use. The LiF and NaCl samples were annealed under vacuum at 600 K during chamber bakeout and for 12 hours directly after baking. It has been reported that annealing at 600 K removes F-centre defects from LiF. The MgO samples were heated at 400 K while baking out the chamber to reduce contamination of the surface during the bake. After cooling the chamber, the sample was then annealed at 950-1000 K in 2×10⁻⁵ torr O₂ (Matheson UHP) for 2 hours. Previous studies have shown that this procedure is effective in removing oxygen deficiencies as well as carbon contamination from MgO. Magnesium oxide surfaces prepared in this way have been shown to have sharp helium-diffraction patterns.
The methyl bromide (Matheson 99.5%) was used without further purification. Gas was dosed onto the cold surface from a glass manifold that was filled from a lecture bottle of CH₃Br to a pressure of 50 torr after first flushing the rack 3 times with 50 torr. Gas from the manifold was introduced into the chamber through a leak valve. Pressure in the chamber was monitored with an ionisation gauge (Varian head, Granville-Phillips 350 controller) and set at a constant value so that the time to achieve the desired dose was approx. 100 s. The output from the ionisation gauge controller was digitised by the SR245 ADC and read by a Labview program which monitored the dose. Very accurate dosing was possible with this program: deviations of the areas of TPD profiles for equivalent doses were typically <5%. The doses in this work are reported in units of Langmuirs (L), where 1 L = a dose of 1x10⁻⁶ torr for 1 s.

2.2 Experimental Procedures

Temperature Programmed Desorption

Because of the problems inherent in performing AES for surface chemical analysis (charging of the surface, formation of defects), the surfaces described here were characterised exclusively by temperature program desorption (TPD). TPD gave no information about the substrate surface structure or chemical composition, but did indicate the presence of surface defects which were identified by high-temperature peaks in the TPD profile. Whenever such defects were observed, further annealing was performed to remove them. TPD profiles were often compared to those obtained on previous crystals to determine the reproducibility of the surface preparation technique.
A typical TPD experiment would take 5-10 minutes. The sample was first flash-heated to remove any possible contaminants. For LiF and NaCl, 300 K was sufficient to clean the surface in a reproducible manner, while for MgO, a much higher temperature, 550 K, was needed. Reproducibility in both the TPD and the time-of-flight spectrum determined the flash temperature. The sample was then cooled to <100 K in 2-3 minutes. Dosing of the gas was performed at the lowest temperature achievable, which was typically 90-95 K for the LiF and NaCl experiments and 98-102 K for the MgO work. The higher base temperature for MgO was the result of the addition of (electrically insulating) sapphire spacers between the sample stage and the yoke (fig. 2.2).

Desorption of CH₃Br was monitored by QMS as the surface temperature was ramped in a uniform fashion; i.e., \( T = T_0 + \beta t \), where \( \beta \) is the heating rate (typically 1-5 K\( \cdot \)s\(^{-1}\)), \( t \) is time, \( T \) and \( T_0 \) are the surface temperatures at time \( t \) and time 0, respectively. The signal monitored was generally 15 amu (CH₃), produced by cracking of molecular CH₃Br in the ioniser; 15 amu was preferred over 94 or 96 (the parent ions) because transmission through the quadrupoles is best for low masses, so it provided a better signal than either 94 or 96. A home-built preamplifier with a gain of 10⁷-10¹⁰ V/A boosted the QMS signal, which was then digitised by the SR245 and sent via the General Purpose Interface Bus (GPIB) to the computer. At the same time, the signal from the thermocouple was digitised by a digital volt meter (Fluke 8860A) and sent to the computer on a separate channel of the GPIB. The two signals were read sequentially by the computer, using a Labview program, at a rate of 14 Hz.

The thermocouple reading was converted to a temperature within the computer program by way of a polynomial fit to the calibration data supplied
by Omega.\textsuperscript{22} The program also controlled the heating rate by sending control voltages to the Kepco supply via the SR245 DAC. The control voltages were defined by the user; there was no feedback involved in the ramp-control part of the program. Nevertheless, it was found that the ramps could be made linear and very reproducible. The ramps used in the MgO work were 1.5 $\text{K}\cdot\text{s}^{-1}$ between 110 and 700 K, with a maximum deviation of $\pm10\%$.

The TPD's were used to calibrate the doses, measured in units of L, in terms of monolayers, ML. In general, that could be done if the desorption energy for the first monolayer was sufficiently greater than the desorption energy for the multilayer (i.e. adsorbate-substrate interactions were stronger than adsorbate-adsorbate interactions). If that condition was met separate monolayer and multilayer peaks would be observed in TPD profiles for doses $>1$ ML. This was often the case, and provided a convenient way to calibrate the number of molecular layers in a given dose, assuming that the molecular densities of the first and subsequent layers were the same, and assuming that the molecules adsorbed in a layer-by-layer fashion. In addition to the simple calibration, TPD gives information about the nature of the interactions between adsorbate molecules and the surface.

- \textit{Kinetics of temperature programmed desorption}

The kinetics of TPD are usually described by the Polanyi-Wigner equation:\textsuperscript{58}

\begin{equation}
\frac{d\theta}{dt} = \nu\theta^n \exp \left( - \frac{E_d}{kT} \right)
\end{equation}  

(2.2)
where $\vartheta$ is the molecular coverage of the adsorbate in ML, $v$ is called the frequency factor (typical values $10^{12}$-$10^{14}$ Hz), $E_d$ is the desorption energy, $k$ the Boltzmann constant, and $T$ the surface temperature. The superscript $n$ is called the "order" of desorption.

The Arrhenius form of (2.2) facilitates its physical interpretation. The desorption energy is the barrier to desorption, a measure of the strength of the bond between the adsorbate and the surface, while the frequency factor is identified with the vibrational frequency of the adsorbed species. The $\vartheta^n$ term contains information about the desorption mechanism, analogous to the concentration factors in chemical kinetics expressions. For example, molecular species which desorb upon recombination of dissociated fragments (e.g. $2\text{H(ad)} \rightarrow \text{H}_2\text{(ad)} \rightarrow \text{H}_2\text{(g)}$) usually exhibit second-order ($n=2$) desorption kinetics while desorption of molecules which adsorb molecularly (undissociated) on a substrate is described by first-order ($n=1$) desorption kinetics. At multilayer coverages the desorption order is zero (up to the desorption maximum), a reflection of the fact that removal of the top molecular layer reveals an identical molecular layer, and not a bare substrate surface. Fractional-order desorption kinetics have also been observed and have been ascribed to desorption from the edges of 2-D islands.

Equation (2.2) describes the time ($t$) rate of desorption. Because TPD profiles are usually presented as plots of desorption rate vs. surface temperature, it is more convenient to express the rate in terms of surface temperature ($T$). Using the chain rule, (2.2) can be rewritten as

$$\frac{-d\vartheta}{dt} = -\frac{d\vartheta}{dT} \cdot \frac{dT}{dt} = \vartheta^n v \exp\left(-\frac{E_d}{kT}\right). \quad (2.3)$$
For a linear temperature ramp ($T = T_0 + \beta t$), as for the experiments described here,

$$-\frac{d\theta}{dT} = \frac{\theta^n v}{\beta} \exp\left(-\frac{E_d}{kT}\right)$$  \hspace{1cm} (2.4)

where $\beta$ is the (constant) temperature ramp. If the value of $\theta$ is well known, then equation (2.4) contains three unknowns: $n$, $v$ and $E_d$.

The value of $n$ can often be determined by comparing the shapes of the TPD traces for various initial coverages. For instance, if $E_d$ and $v$ are constant with coverage and temperature, first-order kinetics yields a temperature of maximum desorption that is constant with initial coverage (see below), zero-order kinetics gives traces whose leading edges coincide and whose peaks shift to higher temperatures with increasing initial coverage, while second-order desorption leads to traces whose peaks shift to lower energy with increasing initial coverage (see fig. 2.4).

When $E_d$ and $v$ are not constants, interpretation of the order is more problematical. Figure 2.5 is a TPD simulation of first-order desorption kinetics in which $E_d$ is a function of coverage. As can be seen from the inset of fig. 2.5, the desorption energy decreases smoothly with coverage, as might be expected from repulsive interactions between adsorbates. The TPD profiles appear distorted compared to the first-order spectra in fig. 2.4(a). The temperature of maximum desorption in fig. 2.5 decreases with coverage. Such behaviour, usually associated with second-order desorption (fig. 2.4(b)), may lead to erroneous assignment of the desorption order.
The frequency factor \((v)\) may be extracted from the leading edge of the TPD profile, without any assumption about the desorption energy (as described below). More commonly, however, \(v\) is assumed (for convenience) to be constant over the TPD peak, with a value in the range \(10^{12}-10^{14}\) Hz (corresponding to ~30-3000 cm\(^{-1}\)). The actual value may be based on the nature of the adsorbate bond; vibrational frequencies in the range \(10^{13}-10^{14}\) Hz (300-3000 cm\(^{-1}\)) would be expected for chemically-bound species, while frequencies of the order \(10^{12}\) Hz would be more likely for physisorbed species. If the desorption energy is assumed not to be constant then the frequency factor should not be a constant, either, since the latter is identified with the vibrational frequency of a molecule in an adsorption well of depth, \(E_d\).

- **The Redhead equation**

TPD is used most commonly in surface science to obtain an estimate of the energy barrier to desorption. In the case of first-order desorption, the desorption energy can be obtained from the peak temperature of the TPD profile by the method of Redhead.\(^{58}\) For this method, \(E_d\) is assumed constant with coverage and temperature. Setting \(n=1\), the peak in (2.4) can be determined from the first derivative:

\[
\frac{dr}{dT} = r \cdot \left\{ \frac{E_d}{kT^2} - \frac{v}{\beta} \exp\left( - \frac{E_d}{kT} \right) \right\}
\]

(2.5)

where \(r\) is the desorption rate, \(r = -\frac{d\theta}{dT}\). Setting (2.5) to zero, the rate of desorption is a minimum when \(r = 0\) (i.e., when \(T=0\) or \(\theta=0\)) and a maximum when
Figure 2.4: Simulations of (a) first-order, (b) second-order, and (c) zero-order temperature programmed desorption profiles for initial coverages of 0.2, 0.4, 0.6, 0.8, and 1.0 ML. For all TPD's shown, $E_d=0.3$ eV, $v=1\times10^{-12}$ Hz, $\beta=1$ K s$^{-1}$. 
Figure 2.5: TPD simulations for first-order desorption kinetics with $E_d$ a decreasing function of coverage. Coverage range. 0.1-1.0 ML; $\beta=1$ K s$^{-1}$; $v=1\times10^{-12}$ Hz; $E_d/eV=0.3-\exp(-\theta/0.5)$. 
\[ \frac{E_d}{kT_p} \cdot \frac{\nu}{\beta} \exp\left(-\frac{E_d}{kT_p}\right) = 0 \]  

(2.6)

Note that the temperature of maximum desorption, \( T_p \), is independent of coverage when \( E_d \) and \( \nu \) are constants, as mentioned above. Rearranging (2.6),

\[ \frac{E_d}{kT_p} = \ln\left(\frac{\nu T_p}{\beta}\right) + \ln\left(\frac{kT_p}{E_d}\right) \]  

(2.7)

Equation (2.7) can be used to calculate \( E_d \) iteratively, assuming a reasonable value for \( \nu \) (10\(^{12}\)-10\(^{14}\) Hz, see above). Because plots of \( E_d \) vs \( T_p \) have been found to be nearly linear, equation (2.7) is more commonly applied with an estimate of \( kT_p/E_d \):

\[ \frac{E_d}{kT_p} = \ln\left(\frac{\nu T_p}{\beta}\right) - 3.64 \]  

(2.8)

Equation (2.8) is known as the Redhead equation; it has been found to provide values of \( E_d \) that are within 1.5\% of those from (2.7), provided \( \nu/\beta \) is between 10\(^8\) and 10\(^{13}\) K\(^{-1}\).\(^{58}\) It is interesting that at the peak in the desorption profile \( (T_p) \) the adsorbate molecules could be considered to be rather tightly bound to the surface--\( E_d/kT_p = 38.1 \), according to (2.8)--and yet the desorption rate is highest at \( T_p \). This is no mystery; at temperatures near \( T_p \) the small minority of high-energy molecules of the thermal distribution are able to escape the well. As the temperature rises the rate of desorption increases. This desorption causes a depletion of the molecular layer until, at \( T_p \), the high
desorption rate cannot be supported by the number of molecules on the surface, and the rate decreases (observable as the peak in the TPD).

The Redhead equation provides a simple way to obtain $E_d$ from the TPD: the error from the method is $\sim 10\%$. Two more accurate methods of analysis that were used to determine the desorption energies from the TPD profiles in this work were the leading edge analysis and the so-called "complete," or isosteric, analysis. Similar desorption energies were obtained by all three methods, except where the accuracy of the analysis was limited by the signal-to-noise ratio. (Good descriptions of the three methods used in this work, as well as nine others, can be found in the review by de Jong and Niemantsverdriet.)

**Leading-edge analysis**

The Habenschaden-Küppers, or leading-edge, analysis assumes no knowledge of the frequency factor, $v$, and attempts to extract a value for it and the desorption energy from the high-coverage side of the TPD peak. Equation (2.4) can be written as (after taking ln of both sides)

$$\ln(r) = n \cdot \ln(\vartheta) + \ln\left(\frac{v}{\beta}\right) - \frac{E_d}{k} \cdot \frac{1}{T}$$

where $r = -d\vartheta/dT$. The data from the leading edge of the TPD is plotted as $\ln(r)$ vs $1/T$. The set of data used must be limited to the first few percent of desorption in order that $\vartheta$ remain approximately constant. The energy of desorption is determined from the slope of the line. The frequency factor can be determined from the y-intercept, provided $n$ is known. At coverages $\geq 0.1$ ML, $\ln(\vartheta)$ is $<10\% \ln(v/\beta)$, so $v$ may be determined fairly accurately without
knowledge of n (particularly if \( \delta >> 0.1 \) ML). This method was found to be difficult to apply to TPD's of low doses due to the poorer signal to noise.

- **Isothermic method**

  The 'complete analysis' or 'isosteric' method allows one to determine the desorption energy for a given coverage, \( \delta_0 \), using a series of TPD traces whose initial coverages are greater than \( \delta_0 \). The rate of desorption, \( r_0 \), at \( \delta_0 \) is first determined for each curve in the series. A plot of \( \ln(r_0) \) vs \( 1/T \) is then made. The energy and frequency factor can then determined from the slope and the intercept of (2.9), as in the leading edge analysis. Unlike leading edge analysis, the complete analysis ignores the temperature dependence of \( v \). Its main advantage over leading edge analysis is that it uses data from the whole peak, and not just the rising edge. By exploiting this feature complete analysis has been used, for example, to demonstrate that the single desorption peak observed for SF\(_6\)/NaCl(001) had two desorption energies (i.e. two slopes in the Arrhenius plot). It was surmised that two distinct phases were present the SF\(_6\) layer.\(^{59}\)

  In the experiments described in this thesis, the following experimental considerations were found to be important for the application of complete analysis. (1) The data collection rate had to be fairly high since a point on one TPD profile, corresponding to a certain coverage, might not correspond exactly with a point on another profile. Often linear interpolation was necessary to find the rate of desorption at a given coverage. (2) Desorption energies at high coverages often could not be determined accurately because of overlap of the monolayer and multilayer peaks. It should be recalled that only those TPD's whose initial coverage is greater than the one chosen for analysis can be used
to determine the desorption energy at the analysis coverage. (3) Many TPD's must be taken above the analysis coverage to obtain an accurate result for $E_d$ and $v$.

**Time-of-Flight Mass Spectrometry**

In TOF experiments, CH$_3$Br was dosed onto the cold (90-100 K) surface as previously described. The photolysis laser entered the chamber through a Suprasil window at the top of the chamber. The photofragments then flew the distance from the substrate surface to the ioniser (23.6 cm) where they were ionised, mass selected, and detected at the channeltron. The signals from the channeltron were then amplified, discriminated, and counted by a multichannel scaler. The counts were stored in a memory module which was read by the computer at prescribed intervals. In this work, one TOF spectrum consisted of 240 individual traces of 1 laser pulse each, and represented a total depletion of the surface coverage of approx. 10%.

Alignment of the laser and detector was very important in TOF measurements (especially in angularly-resolved TOF). Alignment of the sample with the QMS line of sight was achieved by shining a white lamp through the view port at the end of the QMS. This produced a nearly circular spot of approx. 0.9 mm diameter on the crystal, the white light having been collimated by the apertures. Using the x, y, and z translators on the manipulator, the sample was then positioned so that the centres of the spot and the sample coincided.

The laser was aligned with the centres of the light spot and the sample. The beam was directed with a 45° dielectric mirror through the entrance
window at the top of the chamber and onto the sample at an incidence angle with respect to the surface normal of 83° for LiF and NaCl and (a better angle of) 96° for MgO. The laser light produced a blue fluorescence upon striking the crystals, probably due to the presence of residual F-centres which were not removed by annealing. The fluorescence served to indicate the position of the beam. When properly aligned, the laser struck the middle of the entrance window and the centre of the crystal and the light spot. As a final check of the alignment, the laser was apertured to approx. 1 mm and the crystal manipulator rotated from 0-60°. During experiments the laser was apertured to 7 mm dia., 2 mm smaller than the size of the disk seen by the QMS with the sample normal to the detection direction.

- **Time through the quadrupole**

  The TOF spectra as measured included the time taken by the ions to travel the length of the quadrupole after ionisation and acceleration by an electrostatic field (usually 50 V). This time can be determined experimentally for residual gas molecules of ~0 initial kinetic energy by pulsing the extractor voltage (with ~10 V) using the bnc connector above the potentiometer marked "Extractor" on the ioniser control unit. The QMS signal at the mass of interest is monitored with a storage oscilloscope as the extractor lens is pulsed. The trace will reveal a reduction in the transmission of ions due to the sudden change in the extractor potential, followed by recovery as the extractor returns to its preset voltage. The time between the drop in signal and recovery is the time needed for ions of that mass to get from the ioniser to the detector. Previously, that time had been calibrated as $t_{\text{quad}}=24.0(m/E_{\text{ion}})^{1/2}$, where $m$ is the mass of the ion in amu, and $E_{\text{ion}}$ was the preset "ion energy," as read from the ioniser controller. Calibrations performed recently confirmed that the
formula quoted above is accurate for $E_{\text{ion}}=50$ V, but that at low ion energies an independent calibration of $t_{\text{quad}}$ should be performed.

Peak shape is often improved by lowering the ion energy. Splitting of the peaks, in particular, is reduced by using low ion energies. It should be borne in mind, though, that the calibration of $t_{\text{quad}}$ is performed on fragments that have $\sim 0$ translational energy, and that in order to calculate an accurate value of $t_{\text{quad}}$ for photofragments the translational energy of these particles should appear in the expression for $t_{\text{quad}}$. This is especially true for the lower ion energies since the fragments can be formed with translational energies $\sim 10\%$ of the ion energy. At 50 V ion energy, fragment translational energies of 3 eV produce an error in $t_{\text{quad}}$ of $\sim 0.5 \mu$s. Since 3 eV was the upper limit of the photofragment translational energies, this correction was ignored for $E_{\text{ion}}=50$ V. For much lower values of $E_{\text{ion}}$ (25 V was used in some of the experiments reported here), the fragment translational energies could not be ignored, and the following formula was used:

$$t_{\text{quad}} = \frac{K}{\sqrt{E_{\text{ion}} + E'_{T}}}$$

(2.10)

where $K$ is a (mass-dependent) constant determined by the calibration described above and $E'_{T}$ is the translational energy of the photofragment. The formula is iterative in that the values of $E'_{T}$ depend on $t_{\text{quad}}$. However, good values of $t_{\text{quad}}$ could be obtained with only one iteration.

- **Ioniser efficiency**

  The TOF spectra also had to be corrected for the efficiency of the axial ioniser. The probability of ionisation in such an ioniser is proportional to the
time spent in the ionisation region. Since faster fragments spend less time in the ioniser than do slow fragments, dividing by the time spent in the ionisation region should correct the distortion in the measured TOF. If the time-of-flight pathlength is \( s \), then the time spent in the ioniser \( (\text{length } d_i) \) by a particle with a time of flight, \( t \), is just \( t d_i/s \), which is proportional to \( t \). Therefore, if \( n(t) \) is a measured spectrum, and \( P(t) \) the probability of a photofragment arriving at time \( t \), then

\[
P(t) \propto \frac{1}{t} \cdot n(t) \tag{2.11}
\]

- **Transformation to translational energy distributions**

Methyl-radical TOF spectra were transformed in this work to the more universal translational energy distributions. By conservation of matter, the number of fragments arriving in a time interval between \( t \) and \( t + dt \) is the same as the number of fragments arriving in a corresponding energy interval between \( E \) and \( E + dE \); i.e.,

\[
P(t) \cdot dt = P(E) \cdot dE \tag{2.12}
\]

By the chain rule

\[
P(t) \cdot dt = P(E) \cdot \frac{dE}{dt} \cdot dt
\]

\[
P(E) = \frac{1}{dE/dt} \cdot P(t) \tag{2.13}
\]

Since the translational energy, \( E \), is related to \( t \) by
\[ E = \frac{1}{2} \cdot m \cdot \left( \frac{s}{t} \right)^2 \quad (2.14) \]

where \( m \) is the mass of the photofragment and \( s \) is the time-of-flight pathlength, \( dE/dt \) is simply \(-ms^2/t^3\), the negative sign arising from the fact that the translational energy decreases with increasing time of flight. Therefore, by (2.13),

\[ P(E) \propto t^3 \cdot P(t) \propto t^2 \cdot n(t) \quad (2.15) \]

The time of flight, \( t \), was transformed into translational energy by (2.14). With \( s=23.6 \text{ cm} \), (2.14) becomes

\[ E/\text{eV} = 288.7 \cdot \frac{m/\text{amu}}{(t/\mu\text{s})^2} \quad (2.16) \]

Because the time-of-flight spectra, \( n(t) \), were collected as histograms with bin widths of equal time intervals (1 \( \mu \text{s} \)) the transformations, (2.15) and (2.16), to energy distributions decreased the signal-to-noise ratio, especially in the low-energy (long times of flight) region. Because of the large values of \( t^2 \) at low translational energies, use of (2.15) greatly amplified the fluctuations in the signal in that region. In addition to that, the data points were unevenly distributed across the energy spectrum because of (2.16), the density of points being high at the low-energy region, and decreasing towards higher energies. (For example, the region from 0 to 0.1 eV contained 800 points, while the remaining 200 points were spread over the energies >0.1 eV.) For this reason, the energy distributions were rebinned into equal-energy (instead of equal-time) intervals of 0.05 or 0.1 eV.
Figure 2.6: Time-of-flight data and manipulations. (a) Raw TOF spectrum of CH$_3$ from 1 ML CH$_3$Br/LiF(001). (b) Transformation of TOF data into the energy domain. (c) Rebinning of the energy distribution (b) into equal-energy increments.
The rebinning procedure was performed with a computer program which integrated the points within the constant-energy bin using the trapezoidal method. Because the data points often did not coincide with the boundaries of the arbitrary energy bins, points at the boundaries were linearly interpolated. The result of the integration was plotted against the energy of the bin. The rebinning procedure did not cause any discernable distortions in the features of the experimental energy distribution, as can be seen in fig. 2.6.

- **Curve fitting**

Separation of the components of photodissociation described in this work was performed on the raw data, \( n(t) \), because of the noise introduced by the transformations. Separation of the components was achieved either by dividing the TOF at the minimum between the channels (i.e. by "dropping a perpendicular") or by fitting to a function of several curves whenever the shapes of the components could be ascertained. In the case of \( \text{CH}_3\text{Br/Mg(001)} \) the components were fit to a function of three curves--two gaussians, and one "shifted Boltzmann" curve:

\[
\begin{align*}
n(t) &= A_0 + A_1 \cdot \exp \left[ -\left( \frac{t - t_1}{\sqrt{2}\sigma_1} \right)^2 \right] + A_2 \cdot \exp \left[ -\left( \frac{t - t_2}{\sqrt{2}\sigma_2} \right)^2 \right] \\
&\quad + \frac{A_3}{t^4} \cdot \exp \left[ -\frac{m}{2kT_3} \left( \frac{s}{t} - v_3 \right) \right]
\end{align*}
\]

Function (2.17) contains 10 adjustable parameters:

- \( A_0 \) is the average of the background counts.
$A_1$, $t_1$, and $\sigma_1$ were the amplitude, position (in the time of flight), and standard deviation (width) of the gaussian fit to the direct (DIR) pathway (as described in Chapter 5).

$A_2$, $t_2$, and $\sigma_2$ were the corresponding parameters of the fit to the indirect(1) (IND(1)) pathway.

$A_3$, $v_3$, and $T_3$ were the amplitude, group velocity, and "temperature" (width) of the shifted-Boltzmann fitted to the indirect(2) (IND(2)) channel.

The shifted Boltzmann curve (term 4 in (2.17)) should not be confused with a Maxwell-Boltzmann distribution function. While the form is similar, the distribution described by the "shifted" functional form is non-thermal for the case that the group velocity is non-zero. (The function reduces to the Boltzmann function when $v_3=0$.) For that reason, the "temperature" obtained from the fit is not a true thermal parameter, but merely a measure of the width of the peak. This is an important point since distributions of photofragments which have undergone collisions are characterised by temperatures higher than those of photofragments which have escaped "cleanly," i.e. without collisions. That might appear counter-intuitive, since collisions tend to reduce the translational energy and hence "cool" the fragments. The shifted Boltzmann distribution has been used to describe the distribution of velocities in a pulsed molecular beam, and may be thought of as a thermal distribution superimposed on a group velocity.
The spectra were fitted by a commercial graphing program (Igor Pro) with a built-in least-squares fitting routine. The values of all the parameters were restricted to positive numbers to ensure that the resulting fits were physically meaningful. Because of the complexity of the fitting function, all the parameters could not be allowed to vary at once. Furthermore, good starting values of the fitting parameters had to be used in order to obtain convergence. For that reason, the following procedure was adopted:

1. $A_0$ was not optimised by the fitting routine, but was assigned a constant value equal to the average of the 30 data points prior to the rising edge of the DIR TOF peak.

2. Initial values for the positions $(t_1,t_2)$ and widths $(\sigma_1,\sigma_2)$ of the DIR and IND(1) peaks were obtained by fitting the difference of two spectra collected on the same day, one of which showed prominent DIR and IND(1) peaks, the other of which did not. The DIR and IND(1) peaks were accentuated in the difference spectrum and well-described by the Gaussian forms in (2.17).

3. Starting values of the IND(2) parameters were obtained by fitting (2.17) to TOF spectra which showed the least DIR and IND(1) intensity (usually those collected near the surface normal or at low coverage), while holding the DIR and IND(1) parameters at the mean of the values obtained by step (2) of the procedure.

Once the initial values of the parameters were obtained, (2.17) was fitted to all the TOF profiles in the set, optimising all parameters except $A_0$. The
values of the parameters were then averaged and the fit performed one more time, optimising only the amplitudes. The fitting procedure as described produced good fits to the data and internally-consistent values for the fitting parameters describing the three channels of the TOF distribution.

- **Geometry: experimental angles and surface directions**

The crystal tilt played a role in the interpretation of the results of these studies. As can be seen from fig. 2.2, the surface normal of the sample was tilted a small angle, $\alpha = 7^\circ$ for NaCl and LiF, $4^\circ$ for MgO, above the plane of detection. That meant that the smallest angle of detection possible for the system was $\alpha$. Furthermore, while the angular distributions in this work are reported as functions of polar angle, $\theta$, they were not measured along a single azimuth, $\phi$, of the surface. The azimuthal angle was a function of the tilt angle, $\alpha$, and the angle of rotation of the sample mount, $\beta$. The angles $\theta$ and $\phi$ are defined pictorially in fig. 2.7. The polar angle is measured between the surface normal and the detection direction, while the azimuthal angle is measured between the projection of the detection vector onto the surface plane and a reference azimuth. In fig. 2.7 the reference azimuth is denoted $-\text{r}$.

The relationships between the crystal Euler angles, $\theta$ and $\phi$, and the tilt and rotation angle, $\alpha$ and $\beta$, are shown schematically in fig. 2.8. The laboratory reference directions are denoted by the x, y, and z axes. The detection direction, which points along the axis of the QMS, is labelled x. The sample mount's rotation axis is z (the laser propagates in the -z direction). The y axis points towards the LEED optics. The x and y axes define the plane of detection.
Figure 2.7: Schematic diagram of the sample surface and directions referred to in the text. The polar angle, \( \theta \), is measured between the surface normal, \( \mathbf{n} \), and the detection vector, \( \mathbf{i} \), which points towards the mass spectrometer. The azimuthal angle, \( \phi \), measured in the plane of the crystal, is the angle between the reference azimuth, \( -\mathbf{r} \), and the projection, \( \mathbf{P}_i \), of \( \mathbf{i} \) onto the surface. The surface normal and azimuths \( \mathbf{q} \) and \( \mathbf{r} \) are all mutually orthogonal. The detection plane is defined by \( \mathbf{q} \) and \( \mathbf{i} \).
Figure 2.8: Diagram showing the relationships between the fixed sample tilt angle, $\alpha$, the measured rotation angle, $\beta$, and the Euler angles, $\theta$ and $\phi$. The laser propagates in the -z direction. The surface azimuth, $q$, is rotated in the plane of detection (the xy plane) for angularly-resolved measurements. For definitions of vectors, see fig. 2.7.
By defining unit vectors \(\mathbf{i}, \mathbf{j},\) and \(\mathbf{k}\) along the laboratory directions \(x\) (detection), \(y\) (LEED) and \(z\) (rotation), it can be seen from fig. 2.8 that the surface unit vectors, \(\mathbf{n}, \mathbf{q}\) and \(\mathbf{r}\), are given by:

\[
\mathbf{n} = \mathbf{i}\cos\alpha \cdot \cos\beta - \mathbf{j}\cos\alpha \cdot \sin\beta + \mathbf{k}\sin\alpha
\]

\[
\mathbf{q} = \mathbf{i}\sin\beta + \mathbf{j}\cos\beta
\]

\[
\mathbf{r} = -\mathbf{i}\sin\alpha \cdot \cos\beta + \mathbf{j}\sin\alpha \cdot \sin\beta + \mathbf{k}\cos\alpha \tag{2.18}
\]

where \(\mathbf{n}\) is the surface normal and \(\mathbf{q}\) and \(\mathbf{r}\) are unit vectors in the surface plane. The vector \(\mathbf{q}\) is chosen to lie along the intersection between the crystal surface plane and plane of detection (the \(xy\) plane), while the vector \(\mathbf{r}\) is orthogonal to \(\mathbf{q}\) and also in the plane of the crystal surface.

The polar angle is the angle between the detection direction (unit vector \(\mathbf{i}\)) and the surface normal (unit vector \(\mathbf{n}\)). The cosine of the angle between \(\mathbf{n}\) and \(\mathbf{i}\) is just

\[
\cos\theta = \mathbf{n} \cdot \mathbf{i} = n_x
\]

\[
\cos\theta = \cos\alpha \cdot \cos\beta
\]

\[
\theta = \cos^{-1}(\cos\alpha \cdot \cos\beta) \tag{2.19}
\]

The azimuthal angle is defined as the angle between the projection of the detection axis (\(x\)) on the surface of the crystal (the \(qr\) plane in fig. 2.8) and a reference azimuth of the surface. The projection onto the \(qr\) plane of the detection unit vector (\(\mathbf{i}\)) is given by
\[ \mathbf{p}_1 = \mathbf{q}(\mathbf{q} \cdot \mathbf{i}) + \mathbf{r}(\mathbf{r} \cdot \mathbf{i}) \]

which is, by (2.18),

\[ \mathbf{p}_1 = \mathbf{q}\sin\beta - \mathbf{r}\sin\alpha \cdot \cos\beta \]

From this last equation it can be seen that at \( \beta = 0 \) the projection of the detection vector lies entirely along the \(-\mathbf{r}\) direction, whereas at \( \beta = 90^\circ \), it lies along the \( \mathbf{q} \) direction. The \(-\mathbf{r}\) direction is therefore chosen as the zero of azimuthal angle. The azimuthal angle as a function of \( \alpha \) and \( \beta \) is then

\[ \phi = \cos^{-1}\left( \frac{-\mathbf{p}_1 \cdot \mathbf{r}}{\|\mathbf{p}_1\|} \right) \]

\[ \phi = \cos^{-1}\left( \frac{\sin\alpha \cdot \cos\beta}{\sqrt{\sin^2\beta + \sin^2\alpha \cdot \cos^2\beta}} \right) \]  
(2.20)

Expressions (2.18) and (2.20) for the polar and azimuthal angles of detection are plotted as functions of rotation angle in fig. 2.9 for the two tilt angles used in this experiment, \( \alpha = 4^\circ \) and \( 7^\circ \). At \( \beta = 0 \), the polar angle, \( \theta \), is identical with \( \alpha \). As \( \beta \) increases, \( \theta \) approaches \( \beta \) asymptotically. It can be seen from this figure that \( \theta \) can never be less than \( \alpha \). Because the angle \( \alpha \) limits the range of polar angles that can be scanned, it is usually kept small.

As mentioned previously, at \( \beta = 0 \) the detector is aligned along the direction \(-\mathbf{r}\), or \( \phi = 0 \). As \( \beta \) is scanned \( \phi \) changes rapidly, eventually converging on \( \mathbf{q} \), which is \( 90^\circ \) from \(-\mathbf{r}\). Because of the square symmetry of the crystal surfaces used in these experiments, azimuths \( 90^\circ \) from each other are equivalent. In these experiments, the \(-\mathbf{r}\) direction was identified with the \([\overline{1}1\overline{1}]\) surface net vector, while the \( \mathbf{q} \) direction was
Figure 2.9: Variation of (a) polar ($\theta$) and (b) azimuthal ($\phi$) angle with sample rotation angle ($\beta$) for sample tilt angles $\alpha=4^\circ$ and $7^\circ$, as used in this work (see text). The dotted line in (a) is $\beta$, included for reference.
[\bar{1}1]. All the \langle11\rangle directions are equivalent and consist of parallel rows of alternating positive and negative charges.

The change in azimuthal angle with rotation angle is greatest near $\beta=0$. If adsorbate molecules are preferentially aligned along certain azimuths, as has been calculated for HBr\textsuperscript{21} and HI\textsuperscript{60} adsorbed on LiF(001), some distortion of the photofragment angular distributions should be expected for small $\beta$. For example, if in an adsorbate layer molecules are aligned preferentially along the \langle11\rangle directions on LiF(001) with a $\cos^5\phi$ distribution, then a deviation of the detector axis of 17$^\circ$ from one of those axes would reduce the signal to 80$\%$ of that from the 'true' azimuth, $\phi=0$. As can be seen from the curves in fig. 2.9, the smaller the tilt angle the faster the azimuthal angle converges on the [\bar{1}1] azimuth. This is another reason why small values of $\alpha$ are preferred.

2.3 Summary

The time-of-flight (TOF) and temperature programmed desorption (TPD) experiments of this thesis were performed in an ultrahigh vacuum chamber. The substrates used were LiF(001), NaCl(001), and MgO(001); their preparation is described in Chapter 2. The TPD experiments were performed to calibrate the dose of CH$_3$Br required for 1 ML and to determine the desorption energies at various coverages on each of the three surfaces. TPD was also be used to determine the presence of defects on the surfaces. The TOF experiments were performed to determine the translational energy distributions and angular distributions of CH$_3$ photofragments of CH$_3$Br(ad). Both TOF and TPD experiments were performed using a commercial quadrupole mass spectrometer.
with a 23.6 cm flight path. Irradiation for the TOF experiments was provided by an excimer laser operated at 193 nm (ArF).
Chapter 3. Photochemistry of CH₃Br/LiF(001)

As mentioned in the Chapter 1, CH₃Br/LiF(001) was one of the first surface-aligned photochemistry studies performed in this laboratory. The system was re-examined at 193 nm because of the differences in the results obtained from this lab. and the lab. of Tabares et al. This chapter covers the 193 nm photodynamics of CH₃Br adsorbed on LiF(001) as studied by angularly resolved time-of-flight mass spectrometry, from submonolayer to multilayer coverages. The major photoreactive pathway was found to be photodissociation (PDIS in fig. 1.1) to form CH₃(g) + Br(ad)/(g), and two channels of PDIS are identified: direct (DIR) and indirect (IND). The DIR CH₃, characterised by a translational energy distribution similar to the gas phase (peak 2.4 eV, FWHM 0.6 eV; cf. fig. 1.2(a)) and anisotropic angular distributions peaked away from the surface normal, is ascribed to CH₃ which escaped without collisions. The peak in the angular distribution of DIR was directly related to the angle at which the Br-C bond was tilted from the normal (in this case, 20°). The IND CH₃ had a 'collisionally relaxed' energy distribution peaked 1.4 eV lower than the DIR, and yet the width of the distribution was similar to that of the DIR, suggesting that the collision which produced them was of a restricted range of geometries (i.e. a surface-aligned collision). At high coverage, the angular distributions of IND photofragments showed a slight peak ca. 20°. This suggested that some of the IND methyls retained their initial Br-C bond orientation despite the loss of 1.4 eV in a strong collision. To explain that observation, it was proposed that a reactive pathway, exchange (EXCH in fig 1.1(a)), was active; i.e., CH₃ + BrCH₃' → CH₃Br + CCH₃'. The presence of DIR and IND methyls will be a common theme in this thesis, and the EXCH pathway is found to be a dominant process in the case of
CH$_3$Br/MgO(001), Chapter 5. A temperature programmed desorption study of CH$_3$Br/LiF(001) is also presented.

3.1 Temperature Programmed Desorption

The CH$_3$Br/LiF(001) surfaces were characterised by temperature programmed desorption (TPD). Figure 3.1(a) shows that at low coverage the peak in the TPD, i.e., the maximum desorption rate, moved to lower temperatures with increasing dose, from 148 K at 0.03 ML to 113 K at 0.33 ML. With further exposure the peak moved to higher temperatures, as shown in figs. 3.1(b) and (c). The appearance of a second peak in the TPD at high coverage due to the start of a second layer of growth, was never observed. It was therefore necessary to find some other way of estimating the dose of CH$_3$Br equivalent to one monolayer.

In Chapter 4, TPD's of CH$_3$Br/NaCl(001) showed separate monolayer and multilayer peaks. Saturation of the monolayer peak on NaCl(001) was obtained with a dose of 3.0 L. This same dose was taken to correspond to 1 ML for the present system. The argument for doing so is set out below.

Scale models based on estimates of the CH$_3$ and Br van der Waals radii (2.0 Å$^{61}$ and 1.79 Å$^{62}$, respectively), literature values of the C-Br bond length (1.86 Å$^{62}$), and substrate unit mesh parameters (NaCl(001): 3.99 Å; LiF(001): 2.84 Å$^{63}$) were constructed. We assumed (as evidenced by the present study) that CH$_3$Br was bound to the surface with its C-Br axis nearly parallel to the surface plane, that the Br atom was over a substrate cation (Na$^+$ or Li$^+$) and
**Figure 3.1:** Temperature program desorption (TPD) of CH$_3$Br from LiF(001). The mass detected was 15 amu (CH$_3^+$). 1 ML = 3.0 L dose (uncorrected for ionisation efficiency of vacuum gauge).
that the CH$_3$ was over a substrate anion (Cl$^-$ or F$^-$). The structures of NaCl(001) and LiF(001) are both square nets. The density of ion pairs on NaCl(001) is 6.28$\times$10$^{14}$ cm$^{-2}$, while on LiF(001) it is 1.24$\times$10$^{15}$ cm$^{-2}$, implying that the surface density of binding sites on LiF(001) is approximately twice that of NaCl(001). However, because of the small size of the LiF(001) unit mesh, the highest molecular density attainable for a commensurate monolayer, without crowding, was 3.1$\times$10$^{14}$ cm$^{-2}$, corresponding to a coverage of 0.25 (1 molecule per 4 ion pairs). The same molecular density was also found for NaCl(001), corresponding to a coverage of 0.50. It appeared reasonable, therefore, that a dose of 3.0 L would correspond to 1 ML CH$_3$Br/LiF(001), as for CH$_3$Br/NaCl(001).

The molecular coverage obtained for the model surfaces discussed above was very similar to the known surface density of the ab plane of a β-phase CH$_3$Br crystal, 3.4$\times$10$^{14}$ cm$^{-2}$. As will be discussed later, the structure of the CH$_3$Br adsorbate on LiF(001) changes with coverage; however, the dose per molecular layer is assumed throughout this paper to be 3.0 L.

The peak of the TPD profiles in fig. 3.1(a), as already noted, tended towards lower temperatures with increasing coverage up to 0.33 ML. The decrease in the adsorbate-substrate binding energy with increasing coverage suggested the presence of repulsive interactions between adsorbate molecules, which increased as the adsorbate molecules became more crowded together. A similar trend in TPD peak desorption temperature with coverage was observed by Lu et al.$^{45}$ for CH$_3$X (X = Cl, Br, I) on GaAs(110), and was ascribed to lateral dipole-dipole repulsions. Such interactions would tend to work against 2-D islanding. Since at low coverage the peak desorption temperature (see fig. 3.1(a)) is 148 K--far higher than for multilayers--it follows that CH$_3$Br is more strongly bound to the substrate
than to other CH₃Br molecules. At coverages less than 0.33 ML the molecules should be well separated and, on average, distributed evenly over the surface.

Above 0.33 ML (figs. 3.1(b) and (c)), the peaks in the TPD spectra moved to higher temperatures with increasing coverage. The tendency to higher desorption temperature (greater heat of adsorption) above 0.33 ML could be due to rearrangement of the adsorbate molecules. It is possible, for example, that some of the molecules which at low coverage had their dipole moments aligned parallel to the surface plane, 'stood up' at higher coverages. That would have allowed an increased number of molecules to bind to the substrate, and would have relieved some of the repulsion between adjacent adsorbate molecules. Evidence for a small, but measureable, minority of molecules in sub-monolayer CH₃Br/LiF(001) with their C-Br bonds oriented close to the surface normal came from the dynamics (fragment translational energy distributions and angular distributions), as discussed below.

At coverages >0.67 ML the leading edges of the peaks lined up, indicative of zero-order desorption kinetics (i.e., the desorption rate was not dependent on coverage), a situation usually associated with multilayers. Zero-order desorption in the sub-monolayer range has been ascribed to the existence of multiple phases on a surface, each with its own desorption energy. At high coverages (> 1 ML), the zero-order desorption kinetics is ascribed to desorption of multilayers, as mentioned previously.
3.2 Time-of-Flight Mass Spectrometry

**Translational Energy Distributions**

Time-of-flight mass-spectrometry experiments were used to obtain a direct measure of the methyl fragment translational energy distribution at detection angles (angle between the detector axis and the surface normal) from 7-60°. Typical time-of-flight profiles and their transformations to an energy scale, for a low coverage of 1.0 ML and a high coverage of 13.3 ML CH₃Br are shown in fig. 3.2. The profiles in fig. 3.2 were collected at a detection angle of 7°. Figs. 3.2(a) and (b) have been normalised in the same way and are directly comparable, as are (a') and (b').

Both energy profiles (figs. 3.2(a') and (b')) show two distinct features, one at high translational energy, centred at 2.4 eV and extending up to 3.0 eV, the other at low translational energy, centered at 1.0 eV. A minimum appears between the two features at about 1.7 eV; this was chosen as the dividing point between the two types of dynamics. Methyl fragments with kinetic energy ≥1.7 eV were termed 'direct' (DIR), while those with energy between 0.2 and 1.7 eV were termed 'indirect' (IND). The sharp rise in yield of CH₃ at <0.2 eV is due to photoejection of intact CH₃Br, followed by dissociation in the ioniser of the mass spectrometer, a channel studied in earlier work in this laboratory (see previous section). This was not included in the peak for IND photodissociation, a process that yields CH₃ by photofragmentation.

The maximum energy available to the nascent methyl radical, E_{TOT}', for gas-phase CH₃Br is:
**Figure 3.2:** Time-of-flight profiles of (a) 13.3 ML and (b) 1.0 ML CH$_3$Br/LiF(001), and the corresponding energy transformations, (a') and (b'). Arrows in (a') and (b') indicate $E_{TOT}'$, the maximum energy available to the CH$_3$ fragment on 193 nm photodissociation (see text).
where \( m_{\text{Br}} \), etc. are the subscripted masses and \( D_0 \) is the dissociation energy of the C-Br bond being broken\(^{36}\). This \( E_{\text{TOT}}' \) corresponded to the high energy maximum of the distributions in fig. 3.2(a') and (b'), and is marked by an arrow in the two panels. The peak in the DIR energy distribution was at 2.4 eV, about 0.6 eV below the maximum energy available to the gas-phase methyl radical, and only 0.1 eV lower than the observed mean translational energy of CH\(_3\) from photolysis of CH\(_3\)Br in the gas phase.\(^{36}\) At 13.3 ML coverage (fig. 3.2(a')), the DIR peak was centered about 2.4 eV with a FWHM of 0.6 eV. Van Veen et al.\(^ {36}\) found the centre of the gas-phase peak (including contributions from the ground state and spin-orbit excited products) to be about 2.5 eV, with a FWHM of 0.5 eV. These results show that the CH\(_3\)Br potential energy surfaces were not strongly perturbed from the gas-phase on adsorption. We therefore identify the DIR peak at 2.4 eV (extending upward to 3.0 eV) with CH\(_3\) fragments ejected directly into the vacuum from the CH\(_3\)Br adlayer. The IND peak, by contrast, is evidence of scattered CH\(_3\) that have lost, on average, 1.4 eV in an inelastic event.

The shape of the IND peak in the energy distribution has implications for the collision dynamics that convert the initial high-energy CH\(_3\) into the 'relaxed,' low-energy CH\(_3\). The IND methyls have lost approximately 1.4 eV of translational energy collisionally, and yet the breadths of the energy distributions in the two peaks, DIR and IND, are very similar. The loss of such a specific amount of energy suggests that the IND peak was not predominantly the result of multiple
collisions, which would have significantly broadened the peak relative to the DIR one. The narrow width of the IND peak also implies that the range of collision geometries was restricted within the adsorbate layer, most likely by the alignment of the adsorbate molecules.

Coverage Dependence of DIR and IND Pathways

The dramatic increase in the DIR channel, as well as the modest decrease in the absolute intensity of IND CH₃ with increased coverage, is evident when figs. 3.2(b') and (a') are compared. The rise in the DIR signal over the IND is accentuated by measuring at 25° off-normal, as this angle was found to be the peak in the DIR fragments' angular distribution (see next section).

Fig. 3.3 shows the coverage dependence of both DIR and IND CH₃ signals in the time-of-flight spectrum at a detection angle of 25°. The IND signal increased rapidly with coverage up to 0.50 ML, after which a modest decline in intensity was observed. Conversely, the DIR signal increased somewhat more slowly at low coverage, but, more strikingly, continued to increase far beyond 0.50 ML, where the IND signal reached its maximum. By 2 ML the DIR signal dominated the IND. By 13 ML, the ratio of DIR:IND was 5.0. Beyond 13 ML the ratio DIR:IND increased slowly with coverage to 5.6 at 33 ML. The coverage dependence of the IND and DIR components of the methyl photofragments reinforces the view that they arise from different dynamical pathways and indicates that the transition from the low coverage pathway dominated by IND CH₃, to the high coverage pathway dominated by DIR CH₃, is a gradual one rather than being due to a phase transition.
Figure 3.3: Coverage dependence of DIR and IND methyl-radical time-of-flight signals detected at 25° to the normal.
\textit{Angular Distributions}

In fig. 3.4, the angular distributions of DIR and IND CH$_3$ are plotted on the same scale for photolysis of (a) high coverage (13.3 ML) and (b) low coverage (1.0 ML) CH$_3$Br. It is evident from this figure that at high coverage the dominant product of photolysis is DIR CH$_3$, whereas at low coverage it is IND, as in figs. 3.2 and 3.3.

The high-coverage DIR angular distribution in fig. 3.4(a) is markedly narrower than that for IND; it peaks at 25° off-normal. In contrast, the corresponding IND angular distribution is broad, with a maximum intensity near normal, and a roughly $\cos^2(\Theta')$, where $\Theta'$ is the detection angle. The breadths of the angular distributions suggest that the DIR fragments were ejected without collisions (narrow angular distributions), whereas the IND fragments suffered collisions as they left the surface, and so were scattered over a wide range of angles.

The high-coverage DIR angular distribution as measured appeared to have two maxima, one at 25° off-normal, the other near normal. (Angles <7° could not be observed in this experiment, as previously explained.) The rise near normal is, however, explainable as an artifact of the experimental geometry. Because of the tilt of the sample with respect to the detection plane, both the azimuthal and polar angles changed in a reproducible way as the detection angle was scanned (see Chapter 2).

The experimental angular distribution could be well fitted to a product of two gaussian distributions, one in the polar angle, $\Theta'$, the other in the azimuthal
Figure 3.4: Measured DIR and IND CH$_3$ angular distributions for (a) 13.3 ML and (b) 1.0 ML CH$_3$Br. The dashed curve in (a) is a best fit to the DIR data, representing the purely polar CH$_3$ angular distribution, P($\theta'$), along the [11] azimuth (see text).
angle, $\phi'$. The total distribution function in $\theta'$ and $\phi'$ used to obtain this fit had three adjustable parameters: the center of the gaussian in $\theta'$, symbolised $\theta'_0$, and the widths of the gaussians in $\theta'$ and $\phi'$, termed $\sigma_1$ and $\sigma_2$ respectively. The distribution in $\phi'$ was a sum of gaussians whose centers were fixed along the $<11>$ directions of LiF(001). The total distribution function assumed an adsorbate geometry in which the C-Br axes of the CH$_3$Br molecules were tilted at an angle $\theta'_0$ from the surface normal and the projections of the C-Br axes lay along the $<11>$ azimuths.

The dashed line in fig. 3.4(a) is a best fit to the DIR data for 13.3 ML coverage and represents the purely polar angular distribution, $P(\theta')$, of DIR CH$_3$ along only one of the $<11>$ azimuths. The peak in this polar angular distribution, $\theta'_0$, was 20.3°, and its width, $\sigma_1$, was 9.4°. The width, $\sigma_2$, found for the azimuthal part of the distribution function (not shown) was 21.8°, about twice that of the polar part. The angular distributions of the IND channel were unlikely to be affected by changes in the azimuth since the collisions suffered by the IND CH$_3$ would scatter them into a nearly isotropic azimuthal distribution.

Because the DIR fragments suffered no collisions on escape, their angular distribution directly reflected the orientation of the CH$_3$Br molecules in the high-coverage layer. In order to avoid collisions, the molecules which produced the DIR fragments must have been aligned with their C-Br axes nearly parallel or antiparallel to one another, with a CH$_3$ group pointing away from the surface. In addition the DIR fragments, in order to escape cleanly, must have originated in the topmost molecular layer. The peak of the purely polar DIR angular distribution, $P(\theta')$, was at $\theta' = 20°$. This gives the tilt angle of the C-Br axis away from the surface normal. It is significant that this angle is not far from 0°; the
greater the angle the greater the percentage of IND encounters expected within the top layers of adsorbate. Since DIR/IND at 13.3 ML and \( \Theta' = 25^\circ \) is 5.0, the tilt must be slight.

The structure of the \( \beta \)-phase CH\(_3\)Br crystal\(^{62}\) fulfills the criteria mentioned above for the high coverage structure. Molecules in the \( ab \) plane of \( \beta \)-CH\(_3\)Br(s) are aligned with their C-Br axes angled 25\(^\circ\) from the \( c \) crystal axis and antiparallel with respect to their nearest neighbours. It is likely that the high-coverage CH\(_3\)Br/LiF(001) structure, producing mainly DIR CH\(_3\), was very similar to that of the \( \beta \)-phase crystal for two reasons. (1) The peak in the polar fit to the DIR angular distribution is 20\(^\circ\), close to the 25\(^\circ\) angle which the C-Br axis of CH\(_3\)Br makes with the \( c \) axis of the \( \beta \)-phase CH\(_3\)Br crystal.\(^{62} \) (2) The \( \beta \)-phase crystal is an orthorhombic structure (\( a \neq b \neq c \)), and the fit to the experimental angular distribution suggested that the CH\(_3\)Br molecules librated more freely in the azimuthal direction than in the polar direction (\( \sigma_1 = 9.4^\circ \), while \( \sigma_2 = 21.8^\circ \)). Such an anisotropic libration potential is consistent with a structure in which the molecules are spaced farther apart in one direction than in another: i.e., \( a \neq b \).

At low coverage (fig.3.4(b)), the IND photofragments dominated the time-of-flight spectra. The distribution of IND CH\(_3\) at 1.0 ML was approximately \( \cos^{1.4} \Theta' \). The DIR component of the angular distribution shown in fig. 3.4(b) for high coverage appears similar to the one in fig. 3.4(a), but with substantially lower intensity. It seems that the other CH\(_3\) photofragments escaping from the low-coverage CH\(_3\)Br/LiF(001) layer, which comprised the majority, suffered a collision which robbed them of their DIR energy and directionality. As mentioned previously, the TPD results tended to support a model of the low-coverage CH\(_3\)Br/LiF(001) layer in which the molecules were evenly distributed over the
Figure 3.5: Angular distributions of IND CH₃ fragments from (a) 13.3, (b) 1.7, (c) 1.0, and (d) 0.33 ML CH₃Br. The arrows at 25° represent the peak in the measured DIR angular distribution. Dashed lines in (a) and (b) are best fits to cosⁿθ', n=0.8 for 0.33 ML and 1.4 for 1.0 ML. The dashed lines in (c) and (d) have not been fitted to the points.
surface. Since the departing CH₃ fragments usually collided with neighbouring CH₃Br molecules in the low coverage (IND) regime, it is most likely that the C-Br axes of the low-coverage CH₃Br molecules lay approximately parallel to the surface plane. Such an orientation has been computed by Watson et al.⁴⁸ and is ascribed to ion-dipole interactions, in which a Li⁺ ion attracts the negative (Br) end of CH₃Br(ad) and a F⁻ ion attracts the positive (CH₃) end (see also ref. 8).

The form of the IND angular distribution changed slightly but significantly with coverage. In fig. 3.5 the IND angular distributions are given for 0.33, 1.0, 1.7, and 13.3 ML. At coverages of 0.33 and 1.0 ML (fig. 3.5(d) and (c)) cosine functions, cosⁿΘ', described the IND angular distributions adequately, with n=0.8 at 0.33 ML, narrowing to n=1.4 at 1.0 ML. At coverages significantly in excess of 1 ML a deviation from the cosine function is evident. There is a suggestion of a peak in P(Θ') in the region of 25°, i.e. coincident with the peak in the DIR angular distribution. It is striking that a detectable fraction of the IND fragments retain some memory of the molecular orientation, despite the fact that the recoiling CH₃ has collided strongly enough with a neighbouring CH₃Br molecule to lose, on average, 1.4 eV of translational energy. With so many degrees of freedom in both collision partners one would expect a wide range of inelastic pathways, leading to loss of initial translational direction.

A possible mechanism that could account for such a retention of memory involves a chemical reaction, in which a CH₃ photofragment produced in the molecular layer just below the top layer encounters the Br end of a CH₃Br molecule in the top layer, forming CH₃Br, and ejecting the CH₃ from the molecule in the top layer in an exchange reaction with inversion of the CH₃ umbrella (see fig. 3.6(a)): 
\[ \text{CH}_3 + \text{BrCH}_3' \rightarrow \text{CH}_3\text{Br} + \text{CH}_3' \]  \hspace{2cm} (1)

In such a scheme, much of the translational energy in the original CH\(_3\) photofragment would be lost to inversion modes of the free CH\(_3'\) as well as to vibration in the CH\(_3\)Br, and yet the alignment of the molecule under attack would be evident in the direction of the ejected radical. In Chapter 5, reporting experiments on the related system CH\(_3\)Br/MgO(001), we shall give strong evidence for reaction (1) as a major pathway for translational energy loss. The evidence consists of a marked peak in the inelastic angular distribution along the Br-CH\(_3\) bond direction. We previously noted the occurrence of this general type of exchange, with retention of the memory of the bond axis of the molecule under attack, in a theoretical study of the simpler surface-aligned photoreaction. H + BrH' \rightarrow HBr + H'.\(^{24}\)

While the DIR channel is primarily associated with multilayers of CH\(_3\)Br, DIR photofragments were observed at coverages as low as 0.17 ML where the DIR peak accounted for ~10% of the time-of-flight intensity (see fig. 3.3). Hence, even at very low coverage a fraction of the CH\(_3\)Br molecules were aligned with their C-Br axes close to the surface normal and methyl pointing up. Those molecules could act as nucleation sites for growth of the high-coverage, 'standing-up,' structure.

As is evident in figs. 3.2, 3.3, and 3.4, the DIR fragments eventually dominated the time-of-flight spectra, but no evidence of a phase transition was observed. The transition from the low-coverage, 'lying-down,' to the high-coverage, 'standing-up' structure appeared to occur by way of a gradual reordering in which the proportion of molecules in the topmost layer whose C-Br axes were aligned close to the surface normal increased continuously.
Figure 3.6: Schematic diagrams of (a) high coverage and (b) low coverage CH$_3$Br/LiF(001).
This re-ordering is represented schematically in fig. 3.6(a). In the bottom-most layer the majority of the CH$_3$Br molecules are forced by the ion-dipole interactions to lie with their C-Br axes near the plane of the LiF(001) surface. A few, however, in response to the intermolecular repulsions evident in the low-coverage TPD's (section 3.1 above), stand up and provide nucleation sites for similarly aligned molecules in the next molecular layer. Eventually, at high coverage, the 'standing-up' phase dominates. In this figure (fig. 3.6(a)) the molecules are represented with a structure similar to that of bulk $\beta$-CH$_3$Br(s). The tilt angle with respect to the surface normal is 20°, as found for the polar angular distribution, and the projections of the C-Br axes in the surface plane are along the $<11>$ azimuths of LiF(001), as assumed in obtaining the polar distribution. The arrows point along the 20° polar angle, and represent the most likely angle for photorecoil of DIR photofragments, and also IND photofragments in the case that the latter result from exchange reaction (see above).

Figure 3.6(b) is a schematic of a low-coverage structure for CH$_3$Br/LiF(001) consistent with the present findings. The molecules lie with their C-Br axes nearly parallel to the surface plane, as suggested by the large preponderance of IND dynamics. The CH$_3$ is above a F$^-$ anion, and the Br above a Li$^+$ cation. The molecules are shown aligned by the surface ions in an orderly array on the LiF(001) surface. Collision geometries between nascent, directed CH$_3$ photofragments and neighbouring CH$_3$Br(ad) molecules are restricted by the surface alignment. The effect of this restricted distribution of collision geometries is to be found in the energy distributions of IND photofragments (fig. 3.2). Despite losing an average of 1.4 eV of translational energy in a strong collision (an amount equivalent to ~15 quanta of the inversion mode of CH$_3$), the IND peaks in the energy distributions are not noticeably broader than the DIR peaks. This
implies a restricted collision geometry. The existence of a single translationally-relaxed peak in the energy distribution, moreover, tends to support a structure with a single collision geometry. A preferred geometry is suggested in fig. 3.6(b). In Chapter 4, on CH$_3$Br/NaCl(001), we report a case where two IND channels, and hence two indirect collision geometries, appear to be operative.

The structure in fig. 3.6(b) restricts the CH$_3$ photofragments to colliding only with the Br end of the adsorbed CH$_3$Br molecules. This geometry would be expected to be highly unfavourable to the production of CH$_4$ by an abstraction reaction. This accords with the fact that CH$_4$(g) was never observed in time-of-flight experiments from submonolayer CH$_3$Br/LiF(001), despite the fact that CH$_3$ radicals are very reactive and undergo collisions with adjacent co-adsorbates with collision energies much in excess of the activation energy for the abstraction reaction, $E_a=0.44$ eV.$^{64}$ (A small amount of CH$_4$(g) was detected in time-of-flight spectra from multilayer coverages, under conditions of high laser fluence and following much signal averaging. The CH$_4$ time-of-flight spectrum exhibited a thermal (Boltzmann) energy distribution with $T=150$ K, only 60 K above the surface temperature. We ascribe this CH$_4$(g) to reaction in the CH$_3$Br matrix to give trapped methane that escaped when the laser radiation partially ablated the matrix.)

3.3 FTIR Results

The results of polarised infrared absorption spectroscopy will be reported for the present system and will soon be released in a paper from this lab.$^{65}$ At low coverage, the infrared absorption results indicated that the average orientation of the CH$_3$Br molecular axis was $63\pm9^\circ$ from the surface normal; i.e., only $27^\circ$ from
the surface plane. This is in qualitative accord with the 'lying down' state inferred from the energy and angular distributions of CH₃ photofragments reported above. At multilayer coverage the polarised infrared absorption gave a markedly different average molecular orientation of 36±5° from the surface normal, i.e. 54° out of the surface plane on the average. This is in agreement with the 'standing-up' structure postulated here for the topmost layer at high coverage (FTIR averages over the depth of the adlayer). The angular distributions of the photofragments in the present study led to a tilt angle for the C-Br axis of θ'=20° from the surface normal in the multilayer. Thus the photochemical study of angularly-resolved time-of-flight mass spectrometry and the polarised infrared absorption spectroscopy both indicated that CH₃Br tends to lie down on the surface at low coverage and stand up at high coverage.

3.4 Comparisons with Previous Work

The time-of-flight mass spectrum of the CH₃Br/LiF(001) system was previously studied by Harrison et al. in this laboratory,⁹ at a photolysis wavelength of 222 nm, and by Tabares et al.²⁵ at 193 nm.

In the earlier work from this laboratory submonolayer TPD experiments showed the same steady downward shift in the peak of the spectrum to lower temperature with increasing coverage that was observed here. This was taken to be evidence that the adsorbate was wetting the surface. The experimental conditions for photolysis used in this former study were, however, very different from those of the present work. In the earlier work performed in this laboratory, continuous background dosing of CH₃Br was employed to dose a crystal cooled to 117 K. Efficient photodesorption (a substrate-mediated process dependent on
crystal purity, and not observed for the crystals in the current work), as well as thermal desorption of CH$_3$Br molecules at 117 K maintained the surface concentration of CH$_3$Br(ad) at a steady state coverage during the continuous dosing. The precise coverage during photolysis could not be ascertained. Nonetheless, it was evident that inelastic processes (termed the IND channel, here) which were important at low coverage, gave way to largely DIR photolysis at high coverage.

The work of Tabares et al.$^{25}$ used known coverages, dosed prior to photolysis, as has been done in the present study. A multilayer (20 ML) dose of CH$_3$Br/LiF(001) was deposited by Tabares et al. at 30 K, in contrast to 90 K used here. Other conditions (a wavelength of 193 nm and in the region of 150 pulses of $<$20 mJ/cm$^2$•pulse$^{-1}$) resembled those in the present experiments. Nonetheless, the results of this prior work differed significantly from ours. Their TPD results did not show the high heat of adsorption we found for low coverage CH$_3$Br; the adsorption energy obtained by analysis of their $<$1 ML TPD spectra was the same as that found for multilayer desorption. Tabares et al. concluded that wetting of the surface did not take place, and that 3D clustering occurred at all coverages. We concur, and ascribe this clustering to their low surface temperature.

In their photolysis studies, performed at high coverage only, Tabares et al. reported only a very broad CH$_3$ translational energy distribution with a maximum energy corresponding to that of the gas phase. As noted in Chapter 1 the differing photodynamics are most probably due to the fact that the 30-K multilayer studied by Tabares et al had a different structure from that studied here at 90 K; disordered in their case, and ordered in ours. The proposal that the surface structure varied with deposition temperature was made previously by Robinson et
al.\textsuperscript{50} to explain the differences between the results of their He-atom diffraction experiments, which showed that the molecules of CH\textsubscript{3}Br wetted the surface of LiF(001) forming an ordered monolayer, and the time-of-flight experiments of Tabares et al., which supported disorder and 3D islanding. The low dosing temperature of Tabares et al. could have prevented surface diffusion by CH\textsubscript{3}Br(ad) causing the adsorbate to remain in a less-than-optimal disordered configuration.

### 3.5 Summary

The photodissociation of CH\textsubscript{3}Br(ad) dosed on LiF(001) at approx. 90 K has been studied using angularly resolved time-of-flight mass spectrometry. A study of the same system in this laboratory using polarised Fourier-transform infrared spectroscopy is reported briefly. The observed translational and angular distributions indicated that the structure of CH\textsubscript{3}Br/LiF(001) changed with coverage from one in which the C-Br axis was aligned roughly parallel to the surface plane, to one in which the C-Br axis of the majority of the adsorbate molecules (80\%) was almost vertically aligned, 20° from the surface normal; changing, therefore, from 'lying down' to 'standing up'. This change in structure was mirrored in the FTIR results.

The high-coverage CH\textsubscript{3} translational energy distribution was dominated by a peak centered at 2.4 eV (similar to that for gas-phase photolysis\textsuperscript{36}) with a FWHM of 0.6 eV, comparable to that in the gas. The angular distribution of this 'direct' (DIR) CH\textsubscript{3} channel was narrow, with a measured peak at Θ'=25° (where Θ' is the experimental detection angle). The energy and angular distributions for this DIR component indicated that the photofragments had left the adsorbate layer without suffering collisions with neighbouring adsorbate molecules. The DIR angular
distribution of high-coverage CH₃Br/LiF(001) was fitted to a product of gaussians in θ' and φ' (the polar and azimuthal angles, respectively). The fit was consistent with a picture in which: (i) the CH₃Br molecules were canted at θ' = 20° from the surface normal, (ii) the molecules were preferentially aligned along the [11] and equivalent azimuths, and (iii) librations in the φ' direction were of higher amplitude than those in the θ' direction. The differing widths in θ' and φ' suggested a high-coverage structure in which CH₃Br/LiF(001) had a rectangular unit mesh comparable to the ab plane of β-CH₃Br(s).

The low-coverage CH₃ translational-energy distributions were dominated by collisionally-slowed CH₃ (termed 'IND', for indirectly scattered), with a peak at 1 eV and a broad (cos⁰·⁸ at 0.33 ML) angular distribution. This coverage-dependent indirect (IND) CH₃ channel is ascribed to a collisional energy-loss of approximately 1.4 eV from methyl radicals initially formed with 2.4 eV of translation (observed for DIR CH₃, and also for direct photodissociation of CH₃Br(g) to give CH₃). The existence of a single collisionally-slowed peak in the energy distribution, at both low and high coverage, with a width not much greater than that of the DIR peak, is noteworthy since a collision strong enough to transfer 1.4 eV into internal excitation of the CH₃ and its collision partner, CH₃Br(ad), would be expected to give a wide range of inelastic outcomes involving the loss of 0-2.4 eV of energy. The restricted outcome observed is indicative of a constrained encounter at both coverages, for example a narrow distribution of collision geometries of the nascent CH₃ with neighbouring CH₃Br(ad) and/or a reactive process that occurs only for well-defined molecular motions.

A (scale) model of the low and high coverage structures (fig. 3.6) suggests that this restricted encounter could be a collinear 'head-to-tail' exchange
reaction, in which nascent CH\textsc{3} collides with the Br end of a neighbouring BrCH\textsc{3}' to form CH\textsc{3}Br and release translationally-cooled CH\textsc{3}'. The methyl inversion can be expected to deposit energy preferentially into CH\textsc{3} umbrella motion of the new BrCH\textsc{3} and that of the escaping CH\textsc{3}', with a corresponding restricted energy loss (observed to be -\Delta E_T=1.4 eV) from translation. In a theoretical study for HBr/LiF(001) it was noted that an exchange reaction caused the recoiling species (H in that case, CH\textsc{3}' here) to move initially along the prior Br-H (or Br-CH\textsc{3}') bond direction. In the present work the methyl angular distribution for the IND scattering at high coverage shows evidence of a peak at \Theta'=25° (\theta'=20°), i.e. along the Br-CH\textsc{3}' bond direction. This would be consistent with exchange as the IND pathway.

The majority of the IND methyl is, however, broadly scattered since CH\textsc{3}' formed in an exchange reaction has a broad enough angular distribution to encounter adjacent CH\textsc{3}Br(ad), in contrast to DIR photolytic bond breaking. Secondary encounters of the escaping IND CH\textsc{3} formed in an exchange reaction will dominate in the 'lying-down' geometry characteristic of low coverage, but less so in the 'standing up' configuration of high coverage. This is suggested by fig. 3.5 which shows some Br-CH\textsc{3} directionality in the IND methyl at high coverage, and is pictured in fig. 3.6(a) which shows 'forward scattered' IND methyl formed by exchange reaction escaping without collision at high coverage, in contrast to low (fig. 3.6(b)). The observed dynamics do not permit us to distinguish between widely-scattered IND CH\textsc{3} coming from exchange reaction, or coming from collisions that fail to result in reaction; accordingly, we have shown both types of events as contributing to IND CH\textsc{3} at high coverage (fig. 3.6(a)) and at low (fig. 3.6(b)).
In summary, we postulate that CH$_3$Br(ad) on LiF(001) can be dissociated to give CH$_3$(g) in two ways: (i) by DIR photodissociation, and (ii) by IND dissociation in which, in some cases, a nascent CH$_3$ with 2.4 eV translation encounters the Br end of an adjacent adsorbate molecule, BrCH$_3$(ad), and liberates CH$_3$' by way of exchange reaction with approx 1 eV of translation and a broadened angular distribution peaked along the prior Br-CH$_3$(ad) bond direction. At high coverage, characterised by a Br-C axis 'standing-up', some of these IND CH$_3$' escape without further collisions, whereas at low coverage (Br-C 'lying down') they do not. The shift from nearly horizontal to nearly vertical geometry with increasing coverage is apparent in a large increase in the observed DIR/IND photodissociation, and also in the polarised FTIR spectra of ref. 65.
Chapter 4. Photodissociation of CH$_3$Br Adsorbed on NaCl(001)

Despite the similarities in the substrates used in the present and preceding chapters (both are square nets with singly-charged anions and cations) the two surfaces produced markedly different desorption characteristics and photodynamics. The TPD of CH$_3$Br/NaCl(001) showed both a monolayer and a multilayer peak, with average adsorption energies of 0.38±0.01 eV and 0.33±0.02 eV, respectively. As in the case of CH$_3$Br/LiF(001), both DIR and IND photodissociation channels are observed. The DIR P($E_{T'}$) was centred at 2.4 eV, indicating that DIR methyls escaped without collisions. The peak in P(θ') of DIR from NaCl(001) was 38° from normal, compared to 25° from LiF(001), indicating different tilt angles for the 'standing up' phases of CH$_3$Br on LiF(001) and NaCl(001). The DIR methyls constituted a minor pathway at all coverages on NaCl(001), whereas on LiF(001) the DIR dominated at multilayer coverages. The P($E_{T'}$) of IND methyls showed two peaks at 1.1 and 0.6 eV. The loss of such specific amounts of translational energy suggests that they were created by two distinct collision events; for example, by end-on and side-on collisions dictated 'collinear' and 'bent' adsorbate geometries. Angular distributions of the IND photofragments were approx. Cos$^{2.7θ'}$. The presence of IND as the major pathway was consistent with a model of the surface structure in which most of the molecules lay on the surface with their Br-C axes nearly parallel to the plane at all coverages. This was confirmed by polarised FTIR.
4.1 Temperature Programmed Desorption

The adsorption behaviour of CH$_3$Br on the NaCl(001) surface was examined by temperature programmed desorption (TPD), monitoring the CH$_3$(g) fragment signal produced by cracking of CH$_3$Br in the mass spectrometer ioniser. The TPD profiles measured at masses corresponding to molecular CH$_3$Br gave identical results but with lower absolute intensity due to formation of fragment ions.

Figure 1 (a) shows TPD profiles for increasing exposures of CH$_3$Br on NaCl(001) up to 40 L (1 L= 1 Torr-s). For CH$_3$Br exposures of $\leq$3.0±0.1 L (uncorrected for ionization efficiency of the vacuum gauge), there was a single peak due to desorption from the first monolayer (ML). A common leading edge was observed for the various submonolayer peaks, i.e. zero order desorption. This unusual behaviour is indicative of complex desorption kinetics involving, for example, two coexisting phases at the desorption temperature.$^{59}$ Further evidence, of such phases will be given below. Similar TPD behaviour has been observed for submonolayer coverages of SF$_6$ adsorbed on NaCl(001)/Ge(100) thin-films$^{59}$ and for C$_2$H$_2$ adsorbed on polycrystalline NaCl.$^{66}$ It was attributed to the coexistence of a two-dimensional lattice-gas adsorbate and an ordered phase.

Exposures of $>$3.0±0.1 L resulted in the apparent saturation of the monolayer desorption peak and the appearance of a second peak at approximately 10 K lower temperature due to formation of the second and subsequent layers. The monolayer feature exhibited a slight increase in intensity ($<$ 5%) during the initial growth of the second layer TPD features which could indicate incomplete saturation of the monolayer or be due to overlap of the monolayer and second layer peaks in the TPD profile. A common
Figure 4.1: Temperature programmed desorption (TPD) profiles of CH$_3$Br(ad) on NaCl(001) at 95 K measured at 15 amu from cracking of CH$_3$Br(g) with a heating rate of 2.5 Ks$^{-1}$. (a) 0.5 L (b) 1.0 L (c) 2.0 L (d) 3.0 L (e) 3.5 L (f) 4.0 L (g) 6.0 L (h) 8.0 L.
leading edge for the desorption profiles, typical of true zero order multilayer desorption, was observed for exposures greater than 3 ML. The features which appeared at >140 K are thought to be due to desorption from the sample mount and the finite pumping speed of the vacuum system.

The TPD profiles gave direct evidence for completion of the first adsorbed monolayer for a CH\textsubscript{3}Br exposure of 3.0±0.1 L in our vacuum system. The activation energy of desorption, E\textsubscript{d}, was estimated using both 'leading edge'\textsuperscript{67} and 'complete' or isosteric analysis\textsuperscript{68} as recommended recently.\textsuperscript{69} Results were similar using both methods. The monolayer and multilayer desorption energies were E\textsubscript{d}=0.38±0.01 eV and 0.33±0.02 eV respectively. The latter corresponds reasonably closely to the heat of sublimation of CH\textsubscript{3}Br(s) for which the published value is 0.25 eV.\textsuperscript{70} There was a linear relationship between the integrated TPD intensity and the CH\textsubscript{3}Br exposure, as shown in fig. 4.1 (b), suggesting non-dissociative adsorption with a constant sticking probability, probably close to unity, for the coverages investigated here of 0.17 to 13.3 ML.

4.2 Time-of-Flight Mass Spectrometry

Translational Energy Distributions

Figure 4.2 (a) shows the part of the CH\textsubscript{3} time-of-flight profile from 0-250 μs, measured at a detection angle Θ=7° from the surface normal, for 13.3 ML (40 L) CH\textsubscript{3}Br adsorbed on NaCl(001). Signal in this time interval was due to CH\textsubscript{3}Br(ad) photodissociation. Features were observed only when the mass spectrometer detected CH\textsubscript{3} photofragments (15 amu) but were absent when the mass spectrometer detected molecular CH\textsubscript{3}Br (94 and 96 amu). The profile
Figure 4.2: (a) TOF profile for CH₃(g) photofragments from photodissociation of 13 ML CH₃Br/NaCl(001), measured at Θ'=7°. (a') Transformation of (a) to translational energy (solid line); gas phase P(E₉') is also shown (dashed).  
(b) TOF profile for CH₃ from photolysis of 1 ML CH₃Br/NaCl(001) at Θ'=7°, and (b') its P(E₉'). The vertical markers at 1.1 and 0.6 eV in the insets (a') and (b') indicate the energies of the IND(1) and IND(2) channels (see text).
showed two peaks: a narrow peak centred at about 40 \(\mu s\) and a broader peak centred at about 60 \(\mu s\) which extended to approximately 200 \(\mu s\).

The onset of a later broad peak, extending from \(-200-1000\ \mu s\) (centred at \(-300\ \mu s\)), is also visible in fig. 4.2(a). This slower peak, which was qualitatively reproduced at masses corresponding to molecular CH\(_3\)Br, was due to desorption of intact CH\(_3\)Br molecules, followed by cracking in the mass spectrometer ioniser. This process, which was termed photoejection (PEJ) in earlier studies,\(^{11}\) was only observed for CH\(_3\)Br coverages on NaCl(001) of >1 ML. Photoejection exhibiting similar coverage dependence has been observed for CH\(_3\)Br on LiF(001),\(^{9,10}\) OCS on LiF(001),\(^{14}\) H\(_2\)S on LiF(001),\(^{11}\) and CH\(_3\)Br on Br/GaAs(110).\(^{71}\) Photoejection is believed to be caused by electronic excitation of underlayer molecules which give rise to ejection of top layer adsorbate \textit{via} electronic-to-translational (E\(\rightarrow\)T) energy transfer i.e. interadsorbate quenching. Photoejection of CH\(_3\)Br(ad) from NaCl(001) will be the subject of a future publication and hence will not be discussed further here.

Transformation of the TOF profile shown in fig. 4.2 (a) into the energy domain by the appropriate Jacobian operator (see Chapter 2), as shown in fig. 4.2 (a') (solid line), gave the CH\(_3\) translational energy distribution, P(E\(_T\)'). The time-to-energy transformation produced data in which equal time increments became unequal energy increments. The data were, therefore, corrected to generate equal energy increments of 0.1 eV ('rebinned'), as previously described. The two photodissociation peaks centred at \(-40\) and \(-60\ \mu s\) corresponded to most probable translational energies of approximately 2.4 eV and 1.1 eV respectively. For multilayer coverages of CH\(_3\)Br(ad) there was a valley between the two peaks, at approximately 1.8 eV. The CH\(_3\) P(E\(_T\)') energy distribution
therefore comprised two channels: one which we have termed the 'direct' (DIR) channel with $E_T > 1.8$ eV and another the 'indirect' (IND) channel with $1.8 \geq E_T \geq 0.15$ eV. The contribution to the CH$_3$ translational energy distribution at $< 0.15$ eV includes CH$_3$(g) from photodissociation and from CH$_3$Br photoejection.

Superimposed upon the 13 ML P(E$_T$') in fig. 4.2 (a'), for comparison, is that obtained by Van Veen et al. from 193 nm photodissociation of CH$_3$Br(g) in a molecular beam (broken line). The DIR channel CH$_3$ corresponded closely with photolysis of CH$_3$Br(g), both as regards mean translational energy (2.5 eV) and width of the energy distribution (FWHM=0.6 eV). This indicated that the DIR channel operative in the adsorbed phase produced CH$_3$(g) (directed CH$_3$) photofragments that escaped from the adlayer without significant translational-energy loss. The most probable alignment and orientation for the CH$_3$Br(ad) molecules that yield DIR CH$_3$ is, therefore, with the C-Br bond axis approximately along the surface normal, with the CH$_3$ group pointing away from the surface.

Figure 4.2 (b) shows the part of the CH$_3$ time-of-flight profile from 0-250 $\mu$s, measured at $\Theta=7^\circ$, for 1 ML (3.0 L) CH$_3$Br(ad) on NaCl(001). The monolayer TOF spectrum commenced at later time than the multilayer spectrum shown in fig. 4.2 (a); the 40 $\mu$s peak observed at 13 ML is absent at 1 ML. Common to both multilayer and monolayer TOF spectra was a peak at approximately 60 $\mu$s. Furthermore, the monolayer TOF spectrum showed evidence for a peak located at approximately 80 $\mu$s. These features are more meaningful in the P(E$_T$') representation shown in the inset.
The inset, fig. 4.2 (b'), shows the CH$_3$ translational energy distribution obtained from the data of fig. 4.2 (b). The two photodissociation peaks centred at about 60 and 80 μs, corresponded to most probable translational energies of approximately 1.1 eV and 0.6 eV respectively. These features will be discussed in terms of the coverage-dependent P(E$_{T'}$) in the following section.

**Coverage Dependence of DIR and IND Channels**

Representative P(E$_{T'}$) for the CH$_3$ photofragments produced from the photodissociation of CH$_3$Br adsorbed on NaCl(001), from submonolayer to multilayer coverage, are shown in fig. 4.3 (those of 13 ML and 1 ML have appeared as insets to the TOF data in fig. 4.2). The methyl translational energy distribution obtained from 13.3 ML of CH$_3$Br adsorbed on NaCl(001), given by the solid line in fig. 4.3 (a), was dominated by the IND channel. A small but significant proportion of the methyl photofragments were formed in the DIR channel at multilayer coverage. The methyl translational energy distribution obtained from ~13 ML of CH$_3$Br adsorbed on a different, but closely related substrate, LiF(001), is shown by the dotted line in fig. 4.3 (a) (both P(E$_{T'}$) have been similarly normalised).

For the LiF(001) surface there were again two channels; IND centred at approximately 1.0 eV, and DIR centred at approximately 2.4 eV (FWHM ~0.6 eV). The peak energy and FWHM for the fastest component, as can be seen from fig. 4.3 (a), closely resemble that for the DIR from CH$_3$Br(ad) on NaCl(001), as well as that from photodissociation of CH$_3$Br(g). We conclude that the DIR channel observed on both substrates is due to a similar process, resembling gas-phase photolysis. In both cases, it appears that the DIR
Figure 4.3: Methyl P(E₀) for (a) 13.3 ML (b) 2.0 ML (c) 1.0 ML (d) 0.67 ML (e) 0.33 ML of CH₃Br/NaCl(001) at Θ' = 7°. The P(E₀) for 13.3 ML CH₃Br/LiF(001) is shown in (a) (dashed). In all cases DIR peaked at 2.4±0.1 eV. The two IND channels, at 1.1 eV and 0.6 eV, are indicated by markers. The vertical line separates the DIR and IND channels. Error bars represent 1 standard deviation and were calculated from the raw data, prior to rebinning.
photodissociation yields methyl radicals that leave the CH$_3$Br(ad) without subsequent collisions. It follows that the CH$_3$Br(ad) yielding DIR CH$_3$(g) must be oriented with its CH$_3$ group upward, and the C-Br bond approximately along the surface normal.

Despite the qualitative similarities, there were quantitative differences between the two substrates. The CH$_3$Br/NaCl(001) system studied in the present work showed a much greater proportion of methyl photofragments in the IND channel, and a correspondingly smaller proportion of methyl photofragments in the DIR channel, than did the CH$_3$Br/LiF(001) system. This was a consequence of the different multilayer structures on these two surfaces, as discussed below.

When the CH$_3$Br coverage on NaCl(001) was reduced to 2.0 ML, as in fig. 4.3 (b), the DIR contribution substantially decreased, whereas IND increased. Methyl radicals were produced almost exclusively by way of the IND channel for all coverages ≤2.0 ML. At 1 and 2 ML, the S/N was sufficient to reveal two peaks, reproducibly, in the IND methyl P(E$_T$'). These two inelastic channels were centred at approximately 1.1 eV and 0.6 eV. The approximate locations of these two IND peaks are indicated by markers labeled (1) and (2) in fig. 4.3. They will subsequently be referred to as IND(1) and IND(2). The FWHM of these two IND features appears to be comparable to that for the DIR channel. coverages <1 ML produced a broad and largely featureless IND P(E$_T$'), as shown in fig. 4.3 (d) and (e) without reproducible structure. It seems likely that the IND(1) and IND(2) features in the IND channel at very low coverages have been obscured by a poor S/N.
Figure 4.4: (a) Coverage dependence of the DIR (triangles) and total IND (circles) intensities measured at Θ' = 7°. Note the breakpoint in both cases in the region of 1.5 ML. (b) The DIR/IND ratio obtained from the coverage dependencies of (a). The straight line is the (linear regression) best fit.
The integrated CH$_3$ intensity in DIR (1.8-3.0 eV) and IND (0.15-1.8 eV) channels are given in fig. 4.4 (a) as a function of CH$_3$Br(ad) coverage (for $\Theta=7^\circ$). The IND signal increased linearly up to 1.5-2 ML, after which it decreased slightly. The DIR signal increased less rapidly than the IND signal up to about 2 ML and, in contrast to the IND channel, continued to increase beyond 2 ML.

Figure 4.4 (b) shows the ratio of the two integrated intensities, DIR/IND. Surprisingly, the ratio rises monotonically despite the clear change in the dependence of IND on coverage at approximately 1.5 ML of CH$_3$Br(ad). This is due to the fact that the increase in the DIR signal at coverages $>$2 ML is markedly less rapid than at lower coverages. Despite the steady rise in DIR/IND with coverage, the IND channel still dominated the CH$_3$ P(E$_T'$) at our highest coverage (13.3 ML); the angle-integrated DIR/IND=0.21. In contrast, the DIR dominated the CH$_3$ P(E$_T'$) for LiF(001) with the angle-integrated DIR/IND=3.3.

Although they have very different dynamics, the DIR and IND channels appear to be linked on the basis of their coverage dependence: both channels increase at first with coverage, with a similar abrupt change in the rate of increase at approximately 1.5 ML, at which coverage a phase change may occur. However, over the greater part of the range of changing coverage, the adsorbate structure is modified gradually in such a way as to continually increase the fraction of CH$_3$Br(ad) pointing its CH$_3$ in the upward direction as coverage increases. Both the gradualness of the structural change and its qualitative nature are in accord with the behaviour reported for the same adsorbate on a different substrate, LiF(001). The difference lies in the extent of the change, which is much less marked in the present case, using NaCl as the substrate. At 13 ML coverage in the previous work, DIR predominated for
LiF(001) (~80 % DIR). Here, it is enhanced relative to low coverage, but still constitutes a minor (~20% DIR) contribution.

A number of previous experimental studies of adsorbate photochemistry have proposed that photofragments with translational energies reduced below that for the gas phase had suffered inelastic collisions within the adlayer.\textsuperscript{7,9,11,17,25,72-74} This interpretation is supported by theoretical work,\textsuperscript{24,34,48,60,75} where mechanisms such as 'caging' and 'chattering' have been proposed to account for the observed inelastic scattering. The result of these types of deactivation processes is a Boltzmann translational energy distribution with a temperature approaching that of the surface. Such distributions have been observed experimentally for CH\textsubscript{3}I(ad) photodissociation on TiO\textsubscript{2}(110)\textsuperscript{74} and LiF(001) surfaces.\textsuperscript{35,72}

The striking aspect of the inelasticity observed in the present study, as in the preceding paper on CH\textsubscript{3}Br/LiF(001), is the loss of well-defined energies in the IND event. In the CH\textsubscript{3}Br/NaCl(001) system presented here, methyl radicals initially produced with approximately 2.4 eV lost, on average, 1.3 eV for the IND(1) channel and 1.8 eV of translational energy for the IND(2) channel. The alignment of CH\textsubscript{3}Br(ad) conducive to CH\textsubscript{3}+CH\textsubscript{3}Br(ad) encounters, is with the C-Br bond axis of the photodissociated molecule approximately parallel to the surface plane. This 'lying down' geometry is, therefore, likely to dominate at both low and high coverage for CH\textsubscript{3}Br/NaCl(001) in contrast to CH\textsubscript{3}Br/LiF(001) for which it no longer dominated at high coverage. As noted in section IV below, polarised infrared absorption spectroscopy, performed in UHV in this laboratory, confirms the qualitative picture of a predominantly lying down geometry at both low and high coverages on NaCl(001).
The appearance of clearly resolved peaks in the IND translational energy distribution, of comparable width to the DIR peak, is evidence that the departing methyl fragments were not thermalised by multiple collisions during escape. Instead, the loss of a defined 1.3 eV or 1.8 eV of translational energy is likely to have occurred in a single collision of specific geometry. Multiple collisions, as noted previously in Chapter 3, would be expected to result in a broad, featureless Boltzmann IND \( P(E_T) \) located at low translational energy.

As in the comparable case of \( \text{CH}_3(g) \) formed from photodissociation of \( \text{CH}_3\text{Br(ad)} \) on \( \text{LiF}(001) \), we have evidence here of a large energy transfer from the recoiling methyl to adjacent \( \text{CH}_3\text{Br(ad)} \). The loss of approximately 1.3 or 1.8 eV of translational energy from \( \text{CH}_3 \) in the IND channel corresponds to many quanta of C-Br vibration in the \( \text{CH}_3\text{Br(ad)} \) collision partner \((v=15 \text{ and } 25 \text{ respectively})\). Energy will also be disposed of concurrently as excitation of the internal modes of the \( \text{CH}_3 \) (each quantum of the \( v_2 \) 'umbrella' mode has an energy of approximately 0.08 eV\(^76\) and perhaps as frustrated translation of the \( \text{CH}_3\text{Br(ad)} \) (i.e. excitation of the adsorbate-substrate bond of up to 0.38 eV if the substrate is \( \text{LiF(s)} \) and up to 0.33 eV if, as at high coverage, it is \( \text{CH}_3\text{Br(s)} \)). It is possible that the collision between \( \text{CH}_3 \) and \( \text{CH}_3\text{Br(ad)} \) contributes to the experimentally observed collisional ejection of \( \text{CH}_3\text{Br(g)} \).

Transfer of small portions of the initial 2.4 eV of translational energy into a variety of degrees of freedom of the collision partner and the \( \text{CH}_3 \) projectile, would be expected to produce a thermal \( P(E_T) \). The appearance of pronounced structure in the IND \( P(E_T) \) suggests that a more specific type of encounter results in the loss of either 1.3 or 1.8 eV, representing considerable percentages of the incident \( \text{CH}_3 \) translational energy (55 % and 75 %, respectively).
Since chemical reaction only occurs for a well-defined class of encounters, it may be that (as in the case of CH₃Br/LiF(001), and as is strongly indicated by the angular distribution of indirect CH₃(g) from CH₃Br/MgO(001); see Chapter 5), the CH₃+CH₃Br(ad) collision that is responsible for loss of a specific amount of translational energy is an 'exchange' reaction:

$$\text{CH}_3 + \text{Br-CH}_3' \rightarrow \text{H}_3\text{C-Br} + \text{CH}_3'$$  \hspace{1cm} (1)

The appearance of two well-defined peaks in the IND P(Eₗ') would be explained if exchange reaction occurred in two different but specified geometries. An obvious pair of geometries for CH₃Br(ad) on a square surface-net would be 'collinear' versus 'bent' (i.e. adjacent molecules with C-Br bond axes at 90° in the latter case). Since the indirect CH₃ is widely scattered in the present instance, rather than appearing along the continuation of the Br-CH₃ bond direction (as for CH₃Br/LiF(001) and CH₃Br/MgO(001)), we do not have specific evidence for the involvement of reaction (1) in the present system, but postulate reaction (1) by analogy with the two other cases studied. The failure of the CH₃' product to escape along the Br-CH₃' bond direction is explained by the predominance of the lying down molecular configurations which cause nascent CH₃' to collide with adjacent adsorbate before leaving the adlayer.

**Angular Distributions**

By integrating the total intensity in both the DIR and IND channels, from 3.0 to 1.8 eV and 1.8 to 0.15 eV respectively, as a function of detection angle, θ', a methyl angular distribution, P(θ'), was obtained. The angular distribution of the DIR and IND channels was measured at three different
coverages as shown in fig. 4.5 (a) and (b) respectively (solid lines and markers). Both fig. 4.5 (a) and (b) have been similarly normalized. The 1.0 ML angular distribution of the DIR channel in fig. 4.5 (a) was broad but showed a slight increase in methyl emission at \( \Theta' = 50^\circ \) detection angle. At 2.0 ML CH\(_3\)Br coverage, a distinct increase in CH\(_3\) emission at \( \Theta' = 30-40^\circ \) detection angle in P(\( \Theta' \)) was observed. This peak continued to grow in intensity up to 13.3 ML, the highest coverage examined in this work, when the maximum was located at \( \Theta' = 38^\circ \) detection angle. In Chapters 2 and 3 it was explained that an instrumental artifact shifts the observed angle \( \Theta' \) to higher values than the true polar scattering angle \( \theta' \). In the present case, the larger peak value of \( \Theta' \) will result in a smaller correction in going to the purely polar angle \( \theta' \) (since rotation of the 'tilted' crystal about the experimental rotation axis at high angles samples a smaller range of azimuthal angles, \( \phi \)). Accordingly we have corrected \( \Theta' = 38^\circ \) by 3° to give \( \theta' = 35^\circ \). This is a negligible correction to the observed peak angle but we have applied it for consistency. The multilayer peak in P(\( \Theta' \)) was asymmetric and distinctly broadened to the low-angle side.

For comparison, the CH\(_3\)Br/LiF(001) P(\( \Theta' \)) is indicated by a dashed line in fig. 4.5 (a). It has been normalised in a similar manner to the CH\(_3\)Br/NaCl(001) data but the LiF(001) data has been divided by 4.0 to fit the same ordinate. The maximum DIR methyl emission for 13 ML CH\(_3\)Br adsorbed on the LiF(001) surface occurred at \( \Theta' = 25^\circ \) detection angle, corresponding to a polar angle of \( \theta' = 20^\circ \), regardless of coverage. As was mentioned above for the CH\(_3\) translational energy distributions, the DIR channel methyl emission is likely associated with CH\(_3\)Br(ad) molecules with their C-Br bond axis close to the surface normal. The 13 ML DIR angular distribution obtained here for
Figure 4.5: (a) $P(\Theta')$ for DIR methyls from photolysis of 13.3 ML (circles), 2.0 ML (squares) and 1.0 ML (triangles) of CH$_3$Br/NaCl(001). The dashed line is $P(\Theta')$ for 13.3 ML CH$_3$Br/LiF(001) ($\times 0.25$). (b) $P(\Theta')$, for IND CH$_3$ from 13.3 ML, 2.0 ML and 1.0 ML of CH$_3$Br/NaCl(001). The dashed line is a best fit to the form $\cos^n \Theta'$, where $n=2.7$. 
NaCl(001) indicates that the most probable angle of the C-Br bond axis is $\theta' = 35^\circ$ away from the surface normal, for approximately 20% of the CH$_3$Br(ad).

The CH$_3$Br/NaCl(001) $P(\Theta')$ is substantially broader than the CH$_3$Br/LiF(001) system when measured under similar experimental conditions (FWHM=14° for CH$_3$Br/LiF(001); FWHM=21° for CH$_3$Br/NaCl(001)). Since this broadening is asymmetric it seems probable that it derives from a superposition of two distributions. The marked asymmetry in the NaCl(001) DIR channel $P(\Theta')$ which produced CH$_3$ with $\Theta'<38^\circ$ appears as a shoulder in the range $\Theta'=20-30^\circ$ which could be due to scattering of CH$_3$ from neighbouring CH$_3$Br molecules with a deflection of the trajectory but without significant translational energy-loss, or to the presence of a component of the CH$_3$Br(ad) with its bond axis closer to the surface normal. We favour the latter explanation. We have already suggested (Chapter 3) that the multilayer structure on LiF(001) is related to the bulk $\beta$-CH$_3$Br(s) in which CH$_3$Br molecules are aligned with their C-Br axes at 25° from the crystal c axis.$^{62}$ It is likely that at very large distances from the alkali halide surface the structure of the CH$_3$Br(ad) multilayer will be independent of the nature of the substrate. Consequently, we expect to find a fraction of the CH$_3$Br(ad) in the uppermost layers tilted at the same angle of 25° to the surface normal. In the previous chapter the angle was found experimentally to be $\Theta'=25^\circ$ with a corrected polar angle $\theta'=20^\circ$. Provisionally, therefore, we ascribe the shoulder on $P(\Theta')$ in the 20-30° range of angles in fig. 4.5 (a) to this bulk-like structure.

Angular distributions, $P(\Theta')$, for the IND channel for various coverages of CH$_3$Br on the NaCl(001) surface are presented in fig. 4.5 (b). At all coverages from 1 to 13 ML, the IND CH$_3$ angular distribution was maximum around the
surface normal and could be fitted by a simple \( \cos^n \theta' \) function. The shape and intensity of the IND angular distribution was approximately constant with \( n=2.7\pm0.2 \), as shown by the dashed line in the fig. 4.5 (b). Although on both LiF(001) and NaCl(001) surfaces the CH\(_3\) angular distribution was well fitted by a \( \cos^n \theta' \) function, on NaCl(001) the shape and intensity of the IND angular distribution was approximately constant with coverage whereas on LiF(001), \( P(\theta') \) narrowed from \( \cos^{0.8} \theta' \) at submonolayer to \( \cos^{2.0} \theta' \) at multilayer coverages.

Comparison of the ordinate of fig. 4.5 (a) and (b) highlights the dominance of the IND channel in the methyl angular and energy distributions on NaCl(001): the DIR channel formed a minor component at all coverages studied in this work. Even at 13 ML CH\(_3\)Br, most methyl radicals escape into the vacuum with substantially reduced translational energy, i.e. following a collision with a coadsorbate which acts as an 'energy sink'. Both the reduced translational energy and the broad \( \cos^n \)-type of the IND channel indicate that the mechanism responsible involves photodissociation of CH\(_3\)Br(ad) molecules with their C-Br bond axis close to the surface plane, followed by collision and/or reaction with neighbouring CH\(_3\)Br molecules. The polarised IR absorption results, summarised in the following section, provide independent evidence for this lying down geometry.

### 4.3 FTIR Results

In a subsequent paper, we shall report in detail the results of a polarised Fourier transform infrared (FTIR) absorption study of the CH\(_3\)Br/NaCl(001)
system. Pertinent results are quoted here since they have a strong bearing on the photodissociation dynamics.

Owing to the fact that the CH$_3$Br adlayer is almost transparent at the wavelengths used in the FTIR work, this technique probes the full adsorbate thickness giving an average bond angle for the layer. For 0.7 ML of CH$_3$Br adsorbed on the NaCl(001) surface, the FTIR work indicated that the average orientation of the CH$_3$Br figure axis was 64±5° from the surface normal (i.e. the C-Br bond axis was lying down, 26±5° from the surface plane). At multilayer coverages, the average CH$_3$Br figure axis was determined to be 68(±3)°, very similar to that measured for the monolayer. The relatively small number of molecules in the multilayer (~20 %) which had bond axes arranged predominantly ~35° and to a minor extent ~20° from the surface normal (see the discussion of the DIR CH$_3$ recoil above), did not significantly alter the average C-Br bond angle as determined by FTIR.

4.4 Structure of the CH$_3$Br/NaCl(001) Adlayer.

In this section we discuss adsorbate structures consistent with the data presented in the translational energy distributions, P(E$_T$'), angular distributions, P(θ'), and FTIR data for CH$_3$Br(ad) photodissociation on NaCl(001).

For 13 ML CH$_3$Br adsorbed on NaCl(001), a minor fraction of the surface molecules were arranged with their molecular axis at θ'=35° from the surface normal. This contrasts with a substantial fraction oriented at θ'=20° from the surface normal observed for the LiF(001) surface. Evidently, the multilayer structures are markedly different for the two surfaces. This difference in
multilayer structure suggests that the lying down phase observed as the predominant one on both substrates at low coverage, propagates strongly into the multilayer regime for the case of NaCl(001) but not LiF(001). This, in turn, suggests a more ordered layer structure on NaCl(001). We have empirical evidence for this in the nature of the monolayer on each substrate. For CH$_3$Br on NaCl(001) almost all the molecules appear to be in the single alignment we have termed lying down. In contrast, for CH$_3$Br on LiF(001) the observation of both DIR and IND components in the photorecoiling CH$_3$, indicates that alignments in the monolayer are mixed between $\sim$30 % DIR ('standing up') and 70 % IND (lying down). It is the more-ordered monolayer on NaCl(001) that exhibits 'memory' of the monolayer out to at least 13 ML.

Figure 4.6 shows a possible arrangement of multilayer CH$_3$Br adsorbed on the NaCl(001) surface, consistent with the data presented in this paper and the FTIR data. The Br$^{5-}$ atom is placed above the cation, Na$^+$, and the C$^{5+}$ atom above the anion, Cl$^-$. At monolayer or lower coverages, the C-Br bond axis was oriented 64$^\circ$5 from the surface normal as determined by FTIR. Subsequent layers are arranged so that the C-Br dipoles are opposed. The majority of the methyl photofragments which escaped subsequent to photodissociation suffered collision and/or reaction with neighbouring CH$_3$Br adsorbates causing the observed reduction in mean translational energy of, on average, 1.3 or 1.8 eV, and a concurrent broadening of the angular distribution for these IND(1) and IND(2) channels. The DIR channel only became significant at many multilayers coverage on NaCl(001); in view of the angular dependence of the DIR CH$_3$ radicals, they must have originated in CH$_3$Br(ad) with their C-Br axes at approximately 35$^\circ$ to the surface normal. The predominance of the IND channel suggests that even in multilayers on
Figure 4.6: An arrangement of multilayer CH\textsubscript{3}Br on the NaCl(001) surface in conformity with the dynamics observed here and FTIR results. At monolayer and multilayer coverages, the majority of molecules are arranged with their C-Br bond axis 64-68° from the surface normal ('lying down') as indicated by polarised FTIR.\textsuperscript{65} The DIR photodissociation channel indicates that at multilayer coverages a small proportion (=20 %) of the molecules have their C-Br axis directed at \approx 35° from the surface normal with the methyl upwards.
NaCl(001), the majority of CH$_3$Br molecules may be oriented with these C-Br axes close to the surface plane. This is in agreement with the polarised FTIR data.

It should be noted that though a large IND contribution can readily be explained by a lying down configuration, this is not a necessary condition for IND CH$_3$ from multilayers. It is necessary for IND CH$_3$ that the recoiling CH$_3$ encounter a 'soft' target, namely a neighbouring adsorbate molecule. For low coverages ($\leq$1 ML) this necessitates a substantial tilt of C-Br away from the normal toward a lying down configuration. However, at >1 ML a photorecoiling CH$_3$ can encounter a neighbouring molecule in the layers above or below, even with the C-Br axis directed along the normal. For the system CH$_3$Br/MgO(001) we have observed a sharp peak in the angular distribution, P(\(\hat{\Theta}'\)), not only for the DIR methyl but also for the IND methyl (see Chapter 5). The peaks correspond closely in their angle to the normal. This is evidence of exchange reaction (reaction (1) above) in which a CH$_3^+$Br-CH$_3$(ad) encounter releases IND CH$_3^+$ along the target molecule Br-C bond direction. At multilayer coverages this IND scattering is observed for molecules that are nearly upright, for the reasons noted above.

Due to the four-fold symmetry of the NaCl(001) surface, it is possible to arrange two neighbouring CH$_3$Br molecules in registry with the surface below so that their dipole moments are aligned in the same direction, or perpendicular to each other, as shown in fig. 4.7 and labeled (a) and (b). We shall refer to these as 'collinear' and 'bent' geometries respectively but it should be noted that unless the C-Br axis is exactly parallel to the surface plane these geometries are not strictly collinear or bent. The case where the dipoles are aligned antiparallel (with two CH$_3$ groups or two Br atoms pointing towards
**Figure 4.7:** A structure of the CH$_3$Br/NaCl(001) monolayer that could account for the observation of two IND channels. The dashed rectangle represents the unit cell obtained from He diffraction studies on the CH$_3$Br/NaCl(001) system. Molecules are arranged 'lying down' (see text) with the C-Br molecular axis in (a) a 'collinear' geometry and (b) a 'bent' geometry, consistent with the observation of IND(1) and IND(2).
each other) is energetically unfavourable. Calculations of the adsorption energies of these three geometries have been performed for the HBr/LiF(001) system. In that case, the adsorption energies of the collinear and bent arrangements were found to differ by only 10 meV, whereas the adsorption energy of the opposed-dipole case was unstable by more than 1.1 eV.

The presence of two different collision geometries for CH₃...Br-CH₃ (where CH₃ with preferred directionality is photorecoiling from an adjacent aligned methyl bromide molecule) provides a plausible explanation for the differing inelastic pathways IND(1) and IND(2). An example of one possible commensurate monolayer structure which accommodates these two geometries is shown in fig. 4.7. This structure is consistent with the dimensions of the CH₃Br/NaCl(001) unit cell, shown by a dashed line in fig. 4.7, determined from He diffraction studies of Robinson et al. Temperature programmed desorption measurements reported in section 4.1 above, already indicated the possibility of two different CH₃Br(ad) phases at coverages up to 1 ML on NaCl(001). This is the region of coverage in which the distinction between IND(1) and IND(2) appears most marked (figs. 2 and 3). It may be that the collinear and bent arrangements predominate in differing coexistent phases.

4.5 Summary

The adsorption and 193 nm photodissociation of CH₃Br(ad) on NaCl(001) has been studied by temperature programmed desorption and by angle-resolved time-of-flight mass spectrometry in ultra-high vacuum. The translational energy and angular distributions of the methyl photofragments indicated that the structure of the CH₃Br(ad) on NaCl(001) did not change
markedly with coverage from <1 to ~13 ML. The C-Br bond axis remained close to the surface plane, in a lying down arrangement. Polarised FTIR data, obtained in the same laboratory, gave this angle as ~64-68° from the surface normal at both submonolayer and multilayer coverages. At multilayer coverages, some direct photodissociation was observed showing that a small proportion (=20 %) of the CH₃Br(ad) molecules were aligned with the C-Br bond axis =35° from the surface normal, and the CH₃ directed upwards. There is also evidence in the angular distribution of CH₃ at multilayer coverages for a small amount of CH₃Br pointing upward at an angle ~25° from the surface normal, characteristic of bulk β-CH₃Br(s).

We have observed three peaks in the CH₃ translational energy distribution, with constant energies but variable peak heights dependent on adsorbate coverage. These peaks were located at approximately 2.4, 1.1 and 0.6 eV. They were termed the direct (DIR) and the two indirect, IND(1) and IND(2), channels, respectively.

The DIR channel, had a similar mean energy and width to that obtained in molecular beam studies of CH₃Br(g) photodissociation. The DIR angular distribution was peaked at ~38° to the surface normal. Both the magnitude of the translational energy and the narrow angular distribution for the DIR channel indicated that those CH₃ products escaped the adlayer without significant energy loss or angular deflection. An entirely comparable DIR channel was observed for the case of CH₃Br/LiF(001) reported in Chapter 3. The difference there was that the DIR channel dominated (80%) and was peaked at ~25° off-normal as in the ab plane of bulk β-CH₃Br(s). The angular distribution of the IND channel was broad (Cos²7θ') and insensitive to coverage from 1-13 ML.
The presence of two collisionally-slowed peaks in the CH₃Br/NaCl(001) IND methyl energy distribution is noteworthy. The nascent CH₃, as evidenced by the DIR channel, has approximately 2.4 eV of translation, as in the gas phase. A sequence of collisions which transferred a total of either 1.3 eV (IND(1)) or 1.8 eV (IND(2)) into internal modes of the nascent CH₃ and its collision partner, would be expected to produce a broad translational energy distribution centred at low energy. The appearance of two IND peaks, each of roughly the same width as the DIR channel, indicates that two different well-defined single collisions were operative between the CH₃ and a CH₃Br(ad) neighbour. The same conclusion was made in regard to the existence of a single IND peak exhibiting a similar energy loss (approximately 1.4 eV) to IND(1) in our study of the CH₃Br/LiF(001) system.

A possible mechanism by which such considerable but restricted fractions of the incident translational energy might be lost to yield the IND(1) and IND(2) channels, would involve a methyl 'exchange' reaction occurring in two different geometries. In such a scheme, photolysis of CH₃Br(ad) with the C-Br bond axis tilted away from the surface normal would produce 2.4 eV CH₃ which encountered the Br end of a neighbouring BrCH₃'(ad) molecule, liberating a new CH₃' radical and forming a new CH₃Br molecule with specific internal excitation characteristic of the 'exchange' dynamics. We proposed this exchange reaction in Chapter 3 to account for the observation of a similarly restricted energy loss from the IND CH₃, and, in that instance, directionality of the IND CH₃. The directionality of the IND CH₃ coming from CH₃Br/LiF(001), though slight, was such as to suggest a preference for CH₃' formation in the IND channel along the prior Br-CH₃' bond direction. The same behaviour will be reported as the major pathway for formation of IND methyl from
CH₃Br/MgO(001) in Chapter 5. The fact that IND methyl shows no such preferred directionality in the present work, is readily explained by subsequent collisions in a system which predominantly 'lies down' at both low and high coverages.

We have proposed a tentative structure for the CH₃Br(ad) monolayer on NaCl(001) which accommodates both a collinear and bent collision geometry to account for the existence of two IND channels. It is consistent with the unit cell dimensions for the CH₃Br/NaCl(001) system as determined by He-atom scattering.⁵₀
Chapter 5. Photodissociation and Exchange Reaction of CH₃Br Adsorbed on MgO(001)

In this chapter a change in substrate to MgO(001) will be shown to affect greatly the photodynamics of CH₃Br. As in the cases of CH₃Br/LiF(001) and CH₃Br/NaCl(001), both DIR and IND photofragments were observed. The DIR methyl translational energy distribution, P(Eₜ'), peaked at 2.3 eV, with a FWHM of 0.65 eV. The IND methyls could be further subdivided into IND(1) and IND(2) peaks, centred at 1.1 and 0.6 eV, respectively. The P(Eₜ') of IND(1) methyls was narrow, ~0.5 eV, while that of IND(2) was ~0.9 eV. At high coverage, 1.5-10 ML, the angular distributions, P(Θ'), for both the DIR and IND(1) methyls were found to be narrow (FWHM ~20°) and peaked at 22°. At low coverage (0.75 ML) the DIR and IND(1) P(Θ') still mirrored each other, but were peaked at ca. 40° and were broader (FWHM ~40°). The change in the DIR P(Θ') with coverage reflected a change in orientation of the molecules. The similarity between the DIR and IND(1) P(Θ') indicated that the IND(1) methyls, despite the loss of 1.2 eV in a strong inelastic encounter, retained the prior Br-C bond directionality. The mechanism attributed to IND(1), which accounts for the retention of direction of methyl with concurrent substantial energy loss, is the exchange reaction proposed in Chapter 3: \( \text{CH}_3 + \text{BrCH}_3' \rightarrow \text{CH}_3\text{Br} + \text{CH}_3' \). The second 'indirect' channel, IND(2), exhibited a somewhat broader translational energy distribution than DIR or IND(1), \( \cos^n \Theta' \) \( (n=2) \), characteristic of strongly inelastic encounters in which memory of the initial CH₃ recoil direction was lost.
5.1 Temperature Programmed Desorption

Temperature programmed desorption (TPD) traces for coverages of 0.06-10.0 monolayers (ML) are shown in fig. 5.1. For this experiment 1 ML = 4.0 langmuirs (L), the dose required to saturate the TPD peak at 122 K. (Langmuirs are uncorrected for ionisation gauge sensitivity, which is 3.7 for CH$_3$Br.$^{77}$ A dose of 1 L is the equivalent of $1\times10^{-6}$ torr for 1 s.) For coverages between 0.06 and 1.0 ML (fig. 5.1(a) and (b)), the TPD behaviour of CH$_3$Br/MgO(001) was very similar to that of CH$_3$Br/LiF(001) (see Chapter 3). For an initial coverage of 0.06 ML the maximum desorption rate was at 148 K. As the initial coverage was increased, the peak shifted to lower temperature, to a minimum value of 122 K at 0.62 ML. According to the Redhead equation$^{58}$ the desorption energy ($E_d$) for CH$_3$Br/MgO(001) changed smoothly from 0.36 eV to 0.30 eV between 0.06 and 0.62 ML (assuming the frequency factor, $v=10^{12}$ Hz). Such behaviour is consistent with repulsive interactions between adsorbate molecules, which tend to cause the adsorbate to wet the surface evenly rather than to form 3D islands. From 0.62 ML to 1.0 ML the desorption rate appeared first order; the peak increased in magnitude and maintained a constant position at 122 K.

From 1.0-2.2 ML (fig. 5.1(b)) the behaviour of CH$_3$Br on MgO(001) was very different from that of CH$_3$Br/LiF(001). While no separate monolayer and multilayer peaks were ever observed in the TPD of CH$_3$Br/LiF(001), the TPD's of CH$_3$Br/MgO(001) from 1.0-2.2 ML showed the appearance of two new peaks at 108 and 115 K ($E_d=0.26$ and 0.28 eV) in addition to the monolayer peak at 122 K. The two peaks grew concurrently between 1.0 and 2.0 ML; the 108 K peak dominated at lower coverages, while the 115 K peak dominated at higher
Figure 5.1: Panels (a)-(c) TPD profiles of CH$_3$Br/MgO(001) for coverages of 0.06-10 ML (1.0 ML=4.0 L). Note the presence of the metastable state indicated in panel (b). The inset in panel (c) indicates that the sticking coefficient was constant with coverage at 100 K.
coverages. At coverages of 2.5 ML and higher (10 ML being the highest coverage studied), the peak at 108 K disappeared, and only the 115 K peak continued to grow. The peak at 108 K was therefore assigned to a metastable adsorption state, perhaps a disordered lattice-gas, while the one at 115 K was assigned to the stable multilayer structure. It was further observed that the metastable peak converted with time to the multilayer peak; at a dose of 1.75 ML approx. 50% of the metastable state converted to the multilayer state in 5 min. at 100 K. Similar metastable adsorption states have been observed in the TPD of CH₃I/TiO₂(110)⁷⁸ and CH₃I/Au(100).⁷⁹

Neglecting the metastable peak, desorption of the second layer (1.0-2.5 ML) of CH₃Br appeared to be first order (the temperature of the multilayer peak is constant with coverage up to 2.5 ML). Between 3.75 and 10.0 ML (fig. 5.1(c)) the desorption mechanism was zero order (the leading edges of the multilayer peaks coincided and the peak shifted to higher temperatures), consistent with desorption from multilayers. The inset in fig. 5.1(c) shows that the total area of the TPD traces increased in direct proportion to the amount of CH₃Br dosed, indicating that the sticking coefficient was constant at 100 K from 0-10 ML coverage.

5.2 Time-of-Flight Mass Spectrometry

Translational Energy Distributions

Two methyl time-of-flight (TOF) spectra are shown in fig. 5.2(a). Both were collected at 4°, the closest angle to the surface normal attainable in this experiment. The dashed spectrum in fig. 5.2(a) was from a coverage of 1.5 ML, while the solid line was from 5.0 ML. Note the appearance of a peak in the
time of flight at about 43 µs, at high coverage; this is termed the direct (DIR) pathway because the mean energy (2.3 eV) and breadth (FWHM=0.65 eV) of this peak is similar to that of methyl from gas-phase photolysis\textsuperscript{36} (peak 2.5 eV; FWHM=0.5 eV); therefore, the DIR methyls could not have suffered strong collisions before escaping the surface.

A shift in the position of the major peak with coverage, from 75 µs at 1.5 ML to 65 µs at 5.0 ML, was also observed. This shift was attributed to the appearance of a new channel, in this work, termed indirect(1) (IND(1)), the term 'indirect' indicating that the CH\textsubscript{3} had not escaped collision-free from the surface, but had undergone a strong inelastic encounter which decreased its translational energy. The IND(1) channel was narrow, spanning only 17 µs at half maximum in fig. 5.2(a).

By contrast, the 1.5 ML spectrum showed a broad peak centred around 75 µs, with a FWHM of 45 µs. Apparently, the CH\textsubscript{3} born from the IND(1) pathway experienced different collision dynamics from those produced in the low-coverage TOF. A third channel for production of CH\textsubscript{3}, termed indirect(2) (IND(2)) was thought to contribute to the broad TOF found at low coverage. Figure 5.2(b) is the difference of the two spectra in 5.2(a). It appears from the difference spectrum that the two pathways for production of CH\textsubscript{3}, DIR and IND(1), were roughly Gaussian in shape.

The DIR peak is already evident in fig. 5.2(a); the subtraction merely enhances it in fig. 5.2(b). The two IND pathways were, however, not resolved from each other, so the subtraction procedure assisted in identifying the shapes and relative magnitudes of the IND peaks. The validity of this
Figure 5.2: (a) TOF spectra of 5.0 ML dose (solid) and a 1.5 ML dose (dotted), both collected at $\Theta'=4^\circ$ (the closest angle to the normal attainable with the experimental apparatus). The shading gives an approximate indication of the three components. Panel (b) shows the difference of the two TOF spectra in panel (a), thereby emphasising the DIR and IND(1) channels.
procedure will be borne out in the angular distributions. As will be seen in the next section, the two IND pathways had very different angular distributions. The IND(1) distributions mirrored those of the DIR, with off-normal peaks, while the IND(2) distributions were broad (roughly $\cos^2\Theta'$) and centred near normal. If the IND(1) and IND(2) methyls had shared a common origin (i.e. suffered the same dynamical encounters) then their angular distributions would have resembled each other.

The DIR and IND(1) pathways were fitted to Gaussian functional forms, whereas the channel termed IND(2) was fitted to a 'shifted Boltzmann' form as described in Chapter 2. The fits were performed on the raw TOF data, before transformation to translational energy distributions. Figure 5.3 shows the translational energy distribution for a 10.0 ML dose, collected at 20°. Dashed lines in fig. 5.3 are energy transformations of the fits to the three channels: DIR, with a peak at 2.3 eV; IND(1), peaked at 1.1 eV; and IND(2), at 0.6 eV. The total fit is also shown. The rise in intensity below 0.1 eV is due to photoejection of intact molecules (followed by cracking to yield CH$_3$ in the QMS ioniser), a dynamical pathway described previously.\textsuperscript{10}

As fig. 5.3 shows, the DIR and IND(1) peaks have similar widths, despite the fact that IND(1) methyls lost 1.2 eV through a strong collision. In fact, the IND(1) distribution appears to be slightly narrower than that of the DIR--0.5 eV compared to 0.65 eV FWHM. This suggests that the collisions which produced IND(1) were highly restricted, involving a very narrow range of collision geometries and specific dynamics (we propose an exchange reaction, below). By contrast, the IND(2) peak was wider (FWHM=0.9 eV) and shifted by 1.6 eV to lower energy than DIR.
Figure 5.3: Methyl photofragment translational energy distribution derived from a TOF spectrum for a dose of 10 ML, collected at Θ'=20°. Data points have been rebinned. Dotted lines are fits to the three components of photodissociation: DIR, IND(1), and IND(2). The total fit is also shown. Full widths at half maximum (FWHM) for all components are indicated by horizontal arrows.
Angular Distributions

Angular distributions, P(θ'), of the three methyl pathways for coverages of 10.0 and 1.5 ML are given in fig. 5.4. Note the change in the scale of the ordinate in panels (a), (b), and (c) of these figures, showing that the relative amounts of each channel at all coverages studied increased in the order DIR<IND(1)<IND(2).

At all coverages IND(2) was the dominant channel, indicating that most of the departing methyils had undergone strong collisions. In Chapters 3 and 4, such strong inelastic encounters, resulting in broad angular distributions peaked near normal (~cos²θ' in the present case) were attributed to an adsorbate structure in which the C-Br axes of the CH₃Br(ad) molecules lay close to the plane of the substrate crystal. In such a structure the CH₃ departing from a photolysed molecule would strike a neighbouring CH₃Br(ad) before leaving the surface, having its momentum redirected closer to the surface normal, where it would be detected as CH₃(g) leaving the surface. The strong collision suffered by the CH₃ would result principally in the loss of translational energy to the internal modes of the collision partner and the rebounding CH₃. If the momentum of CH₃ is initially directed at ~90° to the normal, 'chattering' (multiple) encounters are likely to be involved (termed '2D caging' in a trajectory study²⁴). The broadly-scattered CH₃ retains no 'memory' of its original C-Br bond direction but is scattered in something approaching a cosine distribution over θ'.

This model was confirmed by polarised fourier-transform infrared spectroscopy (FTIR) measurements performed in this laboratory⁶⁵ on the systems CH₃Br/LiF(001) and CH₃Br/NaCl(001). Both of these systems showed
broadly-scattered, translationally-relaxed CH$_3$ in the TOF, similar in energy loss and angular distribution to that represented by the IND(2) pathway in fig. 5.4. The FTIR spectra indicated that the CH$_3$Br adsorbed on the surface with its C-Br axis $63\pm9^\circ$ from the surface normal at 0.8 ML coverage on LiF(001), and (indistinguishably) $64\pm5^\circ$ at 1 ML coverage on NaCl(001). This was characterised, qualitatively, as a 'lying-down' adsorbate. At high coverage, for the case of LiF(001) with its small unit cell, interadsorbate repulsion caused CH$_3$Br(ad) to 'stand up' on LiF, but not on NaCl. This was, once more, evidenced by the observed dynamics (an increasing proportion of DIR:IND with coverage on LiF) and by FTIR. While FTIR measurements have not yet been performed to determine the tilt of the C-Br axis of CH$_3$Br(ad) on MgO(001), it is likely that the preponderance of IND(2) indicates, as it did in the two previously related systems, that CH$_3$Br adsorbed with its C-Br axis 'lying down'; i.e., at an angle roughly in the surface plane.

The closed circles in fig. 5.4 indicate P($\Theta'$) for the three components of CH$_3$ from 10.0 ML CH$_3$Br/MgO(001). The DIR angular distribution (fig. 5.4(a)) is peaked at 22$^\circ$ with a FWHM of 16$^\circ$. As previously mentioned, the DIR methyls escaped without collisions, so their P($\Theta'$) is a direct measure of the angle between the Br-C bond axis and the surface normal. Thus, the 10-ML DIR angular distribution in fig. 5.4(a) gives evidence of CH$_3$Br(ad) molecules 'standing up' with their Br-C axes aligned 22$^\circ$ from the surface normal. This angle of tilt of the Br-C axes is similar to that found for the 'standing up' phase of multilayers of CH$_3$Br adsorbed on LiF(001), viz 20$^\circ$ (Chapter 3). It is also similar to the angle of 25$^\circ$ between the Br-C bond and the c crystal axis of $\beta$-phase CH$_3$Br(s).62
Figure 5.4: Angular distributions of (a) DIR, (b) IND(1) and (c) IND(2) methyl photofragments from (closed circles) 10 ML and (open circles) 1.5 ML coverage of CH$_3$Br on MgO(001). The broken line in panel (c) gives $\cos^2\Theta'$. 
The angular distribution of the multilayer IND(1) (fig. 5.4(b); filled circles) is very similar to that of DIR; both are narrow (FWHM of the IND(1) P(θ') is 24°) and peaked at 22°, suggesting that DIR and IND(1) share a common dynamical origin. The similar shapes of the IND(1) and DIR P(θ') can be understood in terms of the exchange reaction,

$$\text{CH}_3 + \text{BrCH}_3'(\text{ad}) \longrightarrow \text{CH}_3\text{Br(\text{ad})/(g)} + \text{CH}_3'(\text{g})$$  \hspace{1cm} (5.1)

The nascent methyl, \(\text{CH}_3\), released from a photolysed CH\(_3\)Br undergoes a reactive encounter with the Br end of BrCH\(_3\)'. creating vibrationally hot CH\(_3\)Br, and vibrationally and translationally hot CH\(_3\)'(g), the latter being detected as IND(1). The CH\(_3\)'(g) released will have a lower mean translational energy than the CH\(_3\) which initiated the reaction, due to the vibrational excitation in CH\(_3\)Br and CH\(_3\)'(g). Because chemical reaction requires specific dynamics, the energetics of reaction (1) will be constrained, as evidenced in the P(ET') of IND(1), in fig. 5.3.

The exchange pathway, eq. (5.1), was predicted previously on the basis of trajectory studies on the analogous system HBr(ad)/LiF(001), performed in this laboratory.\(^{24}\). The substrate with its alternating Li\(^+\) and F\(^-\) favours alternation between Br and H in neighbouring dipolar HBr(ad).\(^{21}\) Nascent \(\text{H}\) is predicted to collide at low impact parameter with the Br end of an adjacent BrH' in the adsorbed layer. Trajectories run on a LEPS potential predicted that for these high collision energies exchange (cf. eq. (5.1)) to give HBr and release \(\text{H}'\) with reduced ET' but largely unaltered angular distribution, will constitute a major inelastic pathway. With averaging over collision angles and impact parameters appropriate to an assumed adsorbate temperature of 100 K the
computation predicted a mean energy loss of $\Delta E_T' = 1.1$ eV, and a FWHM breadth of the inelastically scattered $H'$ of $\sim 1$ eV. The case of dipolar $CH_3Br$ adsorbed on a square net (MgO(001)) is expected to be qualitatively similar in its geometry, with a corresponding significant probability for exchange. It is difficult to see how a low impact parameter collision between $CH_3$ and the Br end of $BrCH_3'$ can result in the release of a slowed methyl along the Br-C bond direction unless the colliding $CH_3$ (which cannot pass through the Br target) emerges as $CH_3'$. In the parlance of reaction dynamics, this is the solution to the conundrum of forward scattering at low impact parameter.

An alternative, but implausible, explanation which would account for the directionality of IND(1) involves charge-transfer photodissociation. While the bulk bandgap, determined by optical spectroscopy as $7.77$ eV$^{52}$, is well above the photon energy ($6.42$ eV), a surface band gap of $6.2$ eV has been found for MgO(001).$^{80}$ Charge-transfer photodissociation (CT/PDIS), in which a "hot" electron produced in the conduction band of a metal or semiconductor is transferred to an adsorbate molecule, forming an unstable anion which then dissociates, is well known.$^{5}$ We do not favour this mechanism, however, because the magnitude of IND(1) signal was greater at multilayer coverages ($\leq 10$ ML) than at submonolayer coverage (0.75 ML), in contrast to electron-stimulated processes.

The IND(2) angular distribution is shown in fig. 5.4(c). It is similar for all coverages studied. The distribution is broad (ca. $\cos^2 \Theta'$, FWHM=45°) and centred near normal. This accords with the $P(\Theta')$ found for the IND pathways of $CH_3Br$ on LiF(001) and NaCl(001) (Chapters 3 and 4). Both the broader energy distribution and broad angular distribution obtained for IND(2) would
be expected for strong, non-reactive collisions in view of the range of angles and impact parameters accessible in surface-aligned photochemistry at these substrate temperatures (~100 K). There is no dynamical evidence in the case of IND(2), either in P(E_T') or P(θ'), to suggest that this inelastic pathway can be ascribed to reactive encounters, as was the IND(1) channel.

The open circles in fig. 5.4 give P(θ') for the three channels of CH₃ at a reduced coverage of 1.5 ML. As can be seen, they are very similar to those obtained for the much higher coverage of 10.0 ML, the main difference being a decrease in DIR and corresponding increase in IND(1). The dynamics of CH₃ formation are similar at all coverages ≥1.5 ML, except for the decrease in IND(1) at high coverages.

The angular distributions for DIR, IND(1) and IND(2) at 0.75 ML coverage are presented in fig. 5.5. The shift in the peak of the DIR angular distribution from θ'=22° to ~40°, with concurrent broadening of P(θ') at lower coverage indicates that at reduced coverage the 'standing up' CH₃Br molecules were for the most part tilted twice as far from the surface normal than were their counterparts at higher coverage. This is consistent with the repulsive interactions evident in the TPD at low coverage (fig. 5.1(a)). At lower coverage the molecules tilt farther from the normal before repelling.

It will be noted that in fig. 5.4 a reduction in coverage from 10 ML to 1.5 ML gave no measurable change in the peak DIR tilt angle. It appears that the re-orientation occurs suddenly by way of a phase change between 1.5 and 0.75 ML. It should be born in mind that this 'standing up' structure constitutes on ca. 20% of the adsorbate at 0.75 ML (i.e. the angle-integrated yields of DIR and
IND(1) relative to the total angle-integrated yield from all pathways is ~20\%.
A similar change in structure was observed by Robinson et al.\textsuperscript{50} in a helium
diffraction study of CH\textsubscript{3}Br/NaCl(001). It was, however, not present in our
studies of CH\textsubscript{3}Br adsorbed on the alkali halide substrates, LiF(001) or
NaCl(001).

Most significant in terms of the photodynamics is the fact that the
methyl radicals which have lost \(~1.2\) eV of translational energy, designated
IND(1), exhibited an angular distribution at the reduced coverage of 0.75 ML
(fig. 5.5, panel (b)) that, in common with DIR, shifts from $\Theta' = 22^\circ$ to $\sim 40^\circ$ with a
similar broadening. It is evident that IND(1) is linked to DIR. The Br-C bond
direction undoubtedly governs DIR, and it would seem governs IND(1) as well.
In DIR a methyl radical is ejected along Br-C as a result of the photoexcitation
of a Br-C bonding electron to an antibonding state. In IND(1) a methyl is
ejected by a related process (exchange reaction, eq. (5.1) above) in which the
valence electron of an attacking CH\textsubscript{3} enters the antibonding orbital of Br-C, to
yield a recoiling CH\textsubscript{3}' along the Br-C direction.

5.3 Summary

The adsorption characteristics and 193-nm photodynamics of
CH\textsubscript{3}Br/MgO(001) were studied by temperature program desorption (TPD) and
time of flight (TOF) quadrupole mass spectrometry from submonolayer to
multilayer coverages.
Figure 5.5: Angular distributions of (a) DIR, (b) IND(1) and (c) IND(2) methyl photofragments from a 0.75 ML dose of CH$_3$Br on MgO(001). The broken line in panel (c) gives $\cos^2\Theta'$. 
The TPD profiles up to 1 ML coverage were similar to those found for CH$_3$Br/LiF(001); the peak in the desorption profile shifted to lower temperature with increasing coverage (from 148 K at 0.06 ML, to 122 K at 1.0 ML) suggesting the presence of repulsive interactions between the molecules which would therefore be expected to wet the surface. Above 1 ML, however, the monolayer peak saturated, and two new peaks at 108 and 115 K began to grow. This is in contrast to CH$_3$Br/LiF(001) which showed only one peak at all coverages studied. The two multilayer peaks represented two phases with different desorption energies. It was found that the phase producing the peak at 108 K could be converted into the phase producing the 115 K peak on a time scale of several minutes at 100 K. The peak at 108 K was therefore ascribed to a metastable state, while the one at 115 K was attributed to a stable multilayer.

Time-of-flight profiles for CH$_3$ photofragments revealed three distinct pathways for production of CH$_3$ from CH$_3$Br/MgO(001), which were observed at all coverages studied. These were termed 'direct' (DIR), 'indirect(1)' (IND(1)), and 'indirect(2)' (IND(2)).

The DIR channel had a translational-energy distribution, P(E$_T$'), that was comparable to that of the gas phase. The P(E$_T$') of DIR photofragments was peaked at 2.3 eV with a FWHM of 0.65 eV, compared to the gas-phase peak of 2.5 eV and FWHM of 0.5 eV.$^{36}$ This indicated that the DIR photofragments did not suffer (strong) collisions as they departed from the adsorbate layer. Such fragments could only have been produced by direct photolysis of molecules in the topmost layer of CH$_3$Br, with the CH$_3$ end of the parent molecule pointing toward the vacuum (see fig. 5.6(a)). Angular
Figure 5.6: Schematic diagrams of the dynamics involved in the three photodissociation channels. (a) DIR methyls escaping without collisions with neighbouring adsorbates. (b) IND(1) methyls formed in an exchange reaction, preserving the prior Br-C bond direction. (c) IND(2) methyls undergoing non-reactive collisions (with and without exchange reaction) which broaden their energy and angular distributions.
distributions, \( P(\theta') \), of these photofragments reflected the alignment with respect to the surface normal of the Br-C axes of the parent molecules producing the DIR methyl radicals. At submonolayer coverage the \( P(\theta') \) of these methyl radicals was peaked near 40°, while at coverages >1 ML the peak suddenly shifted to 22°, indicating a change in the structure of the molecules producing the DIR fragments from one in which the Br-C axes were 40° from the surface normal to one with the Br-C axes 22° from the normal.

The IND(1) methyl radicals were peaked at 1.1 eV, 1.2 eV lower in energy than the DIR photoproduct. This shift was attributed to a strong collision suffered by the \( \text{CH}_3 \) on leaving the molecular layer. Despite the strength of the collision, the translational-energy distribution of the IND(1) methyls was very narrow (FWHM=0.5 eV), suggesting that the collision in question occurred under surface-aligned conditions. Further, the IND(1) photofragments showed a similar angular dependence to that of the DIR methyls, being peaked at 40° for low coverage and 22° for high. It follows that the IND(1) methyls maintained a 'memory' of the prior Br-C bond direction, despite having collided strongly enough to lose \((1.2/2.3=)\) 52% of their translational energy. A mechanism which is consistent with both the narrow angular distributions and retention of memory of the prior bond angle for these collisionally-slowed methyls is the exchange reaction,

\[
\text{\text{CH}_3} + \text{BrCH}_3' \rightarrow \text{CH}_3\text{Br} + \text{\hat{CH}_3}'
\]

(see fig. 6(b)). This mechanism was first proposed in a calculation of the analogous system HBr/LiF(001)\(^{24}\) and was used in Chapter 3 to explain similar angular and energy distributions of \( \text{CH}_3 \) photofragments from
CH$_3$Br/LiF(001). At <1 ML coverage the reaction requires that the CH$_3$
photofragment be directed initially approximately in the surface plane so as to
give rise to a low impact-parameter CH$_3$ + BrCH$_3'(\text{ad})$ collisions.

The third channel, IND(2), was broader than IND(1), FWHM of 1 eV, and
peaked at a still lower energy, 0.6 eV. The angular distribution of these methyl
fragments was broad, approx. cos$^2\Theta'$ at all coverages, indicating that they did
not retain a memory of the prior Br-C bond direction. These IND(2) methyls
were attributed to CH$_3$ escaping from CH$_3$Br(ad) with their C-Br bond axes
lying almost in the plane of the surface so as to favour CH$_3$ + adsorbate
collisions, as for submonolayer IND(1). The IND(2) photofragments might also
have undergone an exchange reaction, but subsequent collisions then
broadened the energy distribution and randomised the angles of departure as
illustrated in fig. 6(c).
Chapter 6. Conclusions and Future Directions

Photochemistry of adsorbates is a broad and growing field. This thesis explored the changes that took place in the photodissociation and reaction dynamics of adsorbates on insulator single crystals as the substrate was varied. The crystals studied were LiF, NaCl, and MgO. These have very similar structure. Nonetheless, profound differences were observed in the translational energy distributions and angular distributions of the CH₃ photofragments. The most striking finding presented here is the evidence from the LiF and MgO data of a reactive pathway producing CH₃ in what appears to be an exchange reaction:

\[ \text{CH}_3 + \text{BrCH}_3^{(ad)} \rightarrow \text{CH}_3\text{Br} + \text{CH}_3 \]

6.1 Conclusions

The adsorption and photochemistry of CH₃Br has been studied on several substrates. The substrates, LiF(001), NaCl(001), and MgO(001) were all insulators with square unit meshes. In the bulk, each of the three substrates has a sodium chloride structure. Methyl bromide was chosen as the adsorbate for its high cross-section in the gas phase, and because its gas-phase photodissociation dynamics are well known.

Gas-phase photolysis in the A band of methyl bromide at 193 nm is direct and produces CH₃ + Br\(^{(2P_3/2)}\), Br*\(^{(2P_1/2)}\) via parallel and perpendicular transitions, respectively, in a 4:1 ratio. The methyl radical is born vibrationally excited with an average of 2-4 quanta in the \(v_2\) (umbrella) mode. The possibility of forming either Br or Br*, coupled with the vibrational excitation of the CH₃ leads to a methyl translational energy distribution.
centred at 2.5 eV, with a FWHM of 0.5 eV and a maximum translational energy of 3.0 eV.

The experiments in this thesis were performed in an ultrahigh vacuum chamber equipped with a time-of-flight quadrupole mass spectrometer (QMS). The sample surface normal was tilted 7° above the plane of detection (4° for MgO). It was illuminated at 83° glancing incidence (86° for MgO) along the axis of the rotatable mount by an ArF excimer laser (193 nm). With this experimental arrangement angles of detection between 7° (4° for MgO) and 90° from the surface normal could be attained. The sample was cooled by liquid nitrogen and the CH₃Br dosed by backfilling the chamber to a given pressure for about 100 s.

Temperature programmed desorption (TPD) measurements were performed to determine the dose required for 1 ML, and the desorption energy for each of the surfaces studied. On LiF(001) the desorption energy decreased with coverage from 0.35 to 0.26 eV between 0.03 and 0.3 ML, indicating repulsive interactions. Separate monolayer and multilayer peaks were not observed on LiF, but the repulsive interactions were expected to keep the molecules separated on the surface, at least at low coverage. Separate monolayer and multilayer peaks were observed for NaCl(001); the dose for 1 ML was 3.0 L (Langmuirs). The average adsorption energy of the monolayer peak was 0.38 eV, while that of the multilayer was 0.33 eV. The desorption behaviour in the submonolayer coverage regime on this surface appeared zero-order, perhaps indicating the presence of multiple adsorption phases. At submonolayer coverages CH₃Br on MgO(001) behaved similarly to CH₃Br/LiF(001), with the desorption energy decreasing steadily from 0.36 to 0.30 eV between 0.06 and 0.6
ML. The dose for 1 ML on MgO(001) was 4.0 L. At coverages above 1 ML a multilayer peak appeared with a desorption energy of 0.28 eV. A third peak, with a desorption energy of 0.26 eV, was assigned to a metastable state: it converted to the multilayer peak on a time scale of several minutes.

Both translational energy distributions ($P(E_T')$) and angular distributions ($P(\Theta')$) indicated two distinct pathways for CH$_3$ production on LiF(001), termed direct (DIR) and indirect (IND), and three pathways on NaCl(001) and MgO(001), termed direct (DIR), indirect(1) (IND(1)), and indirect(2) (IND(2)). For all three systems, the DIR methyls had a $P(E_T')$ peaked ca. 2.3-2.4 eV with a FWHM of 0.6 eV, very similar to the gas phase $P(E_T')$: peak 2.5 eV, FWHM 0.5 eV. We conclude that the DIR methyls left the surface without collisions. To achieve this, the methyls had to originate from molecules at the top of the adsorbed layer, with the methyl ends directed towards the vacuum at an angle close to the surface normal. This CH$_3$Br geometry was termed 'standing up'. The IND pathways had translational energy distributions which were lower than the DIR peak by ~1 eV. Despite the large energy loss, indicative of a strong collision, the widths of the IND peaks were very similar to the DIR, suggesting constrained dynamics, due probably to the surface alignment. The IND methyl collision partners were most likely the neighbouring CH$_3$Br(ad). Such collisions are favoured by an adsorbate geometry in which the Br-C axes are directed close to the surface plane, a geometry termed 'lying down' in this work.

Because the impulse of the photodissociation event was directed along the Br-C axis, and because the $P(E_T')$ indicated an absence of collisions with neighbouring adsorbate molecules, the peak in $P(\Theta')$ of DIR methyls indicated
the direction with respect to the surface normal of the Br-C axes of the molecules which produced them. For LiF(001) that angle was 20°, very close to the 25° found for the angle of the Br-C axis to the c crystal axis of β-phase CH₃Br(s). The DIR pathway dominated on LiF(001) at high coverage. It was concluded that the Br-C axes of high-coverage CH₃Br(ad) on LiF(001) were arranged similarly to bulk CH₃Br, i.e. with the Br-C axes antiferral and tilted approx. 25° from the c axis.

On NaCl(001), the Br-C axes were tilted 38° from the normal. The change in the angle of Br-C tilt on going from LiF(001) to NaCl(001) was likely due to the larger unit mesh size of NaCl(001), allowing the 'standing up' molecules to lie farther from the normal. A shoulder in the DIR P(θ') suggested a second phase of 'standing up' CH₃Br/NaCl(001) whose Br-C axes were canted ~25° from the normal, closer to that found for CH₃Br/LiF(001). The DIR channel was always a minor pathway for CH₃Br/NaCl(001), while for CH₃Br/LiF(001) the DIR was dominant at high coverage, and a minor channel at low coverage. The different coverage dependences of DIR methyls from CH₃Br(ad) on the two substrates may be explained by the different unit cell sizes. The 'lying down' structure, associated with the IND photofragments, appeared to befavoured by the larger unit mesh of NaCl(001). The smaller unit mesh of LiF(001) could not accomodate the 'lying down' molecules as well as NaCl(001) could, resulting in a predominantly 'standing up' phase.

The DIR P(θ') for the CH₃Br/MgO(001) system showed that the CH₃Br(ad) underwent a marked change in structure between 0.75 and 1.5 ML. At 0.75 ML the DIR P(θ') was peaked ~40° and was broad, FWHM~40°. Between 0.75 and 1.5 ML the peak in the DIR P(θ') shifted to 22°. The sudden
change in structure may constitute a phase change, although, as was the case of CH₃Br/NaCl(001), the DIR component was a minor one at the lower coverage of 0.75 ML.

At low coverage on LiF(001) the IND peak was dominant, indicating that the low-coverage structure of CH₃Br(ad) promoted collisions between the great majority of CH₃ and adjacent molecules; i.e. the 'lying down' structure. As the coverage was increased, the DIR peak gradually grew in, becoming dominant at multilayer coverages. This was interpreted as a change in the structure of CH₃Br(ad) from a 'lying down' phase to a 'standing up' phase. The change in structure with coverage was confirmed (by other workers in this laboratory) using polarised FTIR. On NaCl(001), the methyl P(Eₚ) was dominated at all coverages by IND photofragments. This implied that CH₃Br(ad) predominantly 'lay down' at all coverages on this substrate. This conclusion was also confirmed by polarised FTIR.

The peak in the IND P(Eₚ) for the system CH₃Br/LiF(001) was 1.0 eV, and its width was 0.9 eV. The small broadening of the IND peak relative to DIR, despite the loss of 1.4 eV in translation to a strong collision, suggested constrained dynamics, probably due to surface alignment. Angular distributions of IND methyls from LiF(001) were broad (∼cos-cos²θ). However, at multilayer coverage a modest peak appeared ca. 25°--near the peak in the DIR P(θ'). This suggested that some of the IND methyls released from LiF(001), despite having lost 1.4 eV in a strong collision, retained some memory of their Br-C bond direction. The mechanism proposed to account for this retention of memory was the exchange reaction:
More striking evidence for this reaction came from CH$_3$Br/MgO(001). The IND(1) pathway in this system had a peak in P(E') at 1.1 eV and a FWHM of ~0.5 eV, approximately the same width as the DIR peak at 2.3 eV, notwithstanding the collisional loss of 1.2 eV. The IND(1) peak was very prominent in the CH$_3$ energy distributions of CH$_3$Br/MgO(001). Angular distributions of IND(1) from MgO(001) mirrored those of DIR at all coverages, despite substantial change in the peak P(θ') with coverage. This indicated that the IND(1) methyls from MgO(001) had, like those from LiF(001), retained memory of the prior Br-C direction, consistent with reaction (6.1). By contrast, the IND(2) peak of MgO(001) was broad and peaked about normal (~cos$^2$θ'), consistent with non-reactive scattering without retention of directionality.

The IND(1) and IND(2) peaks of NaCl(001) were not sufficiently resolved to be separated. While exchange might have been operative in this system, there was no evidence of retention of the bond directionality in the angular distributions. This lack of structure in P(θ') could have been due to secondary collisions of the CH$_3$ released in an exchange reaction. Alternatively, the two peaks evident in the translational energy distributions could have been due to two different non-reactive collisional geometries in which CH$_3$ encountered a neighbouring CH$_3$Br(ad); for instance end-on and side-on geometries. Angular distributions of the two combined IND CH$_3$ channels of NaCl(001) were broad, approximately cos$^2$θ' at all coverages.
6.2 Future Directions

The results of this thesis suggest some interesting experiments. The dynamics of the IND(1) pathway of MgO(001), attributed to the exchange reaction in this work, is, in particular, worthy of further investigation. A study of the internal energy distribution of these methyls may prove informative. Resonance-enhanced multiphoton ionisation (REMPI) has been used to probe the excitation of the $v_2$ (umbrella) mode of CH$_3$ from photolysis of CH$_3$I adsorbed on MgO(001)$^{29}$ and TiO$_2$(110).$^{74}$ In those cases, translationally-relaxed methyls were observed (as in the present study), but the translational energy distributions of the relaxed methyls were thermal, with a temperature comparable to that of the surface. The translationally-relaxed methyls were also found to be vibrationally cooled, the entire population residing in $v_2=0$. By contrast, the IND(1) methyls of the present study, produced by the exchange reaction, should have a non-thermal distribution of vibrational energies. Because the impulse which liberates the IND(1) methyl is directed along the Br-C axis, these methyls should be rotationally 'cool,' though vibrationally 'hot.' In the case of IND(2), where non-reactive collisions are implicated, the rotational excitation would be expected to be greater.

Photochemistry of adsorbates on modified single crystal surfaces is another possible route for exploration. Experiments on LiF(001) surfaces ablated by electron beam irradiation have been performed in this laboratory,$^{14}$ resulting in modified angular distributions. Surfaces created by epitaxy of insulators on conducting substrates$^{81-83}$ are also of interest, since clean, well-ordered surfaces can be made daily. In addition, many surface science techniques which would ordinarily result in charging of the insulator surfaces
could be used to characterise the insulator and adsorbate. Recent reports have suggested other ways of creating 'tailored' substrates. It has been suggested that electron irradiation can be used to create F-centres on the surface of CaF$_2$(111). F-centres have been implicated in a number of phenomena in surface photochemistry, including photodesorption and an increase in the dissociation cross-section of OCS adsorbed on LiF(001). Another group has used an atomic force microscope (AFM) to produce 'hillocks' of NaCl on an NaCl(001) surface in the presence of adsorbed water. While those structures flattened spontaneously, the possibility exists for the creation of a large number of such defects by, for example, using a two-dimensional array of microscopic needles as a template.

In recent years, surface photodynamics has focused on two main classes of systems: adsorbates physisorbed on insulator single crystals and adsorbates physisorbed and chemisorbed on semiconducting or conducting substrates. As mentioned in Chapter 1, the latter systems suffer from a high degree of quenching of the electronic excitation in the adsorbate, and so the photochemistry is usually dominated by the higher-efficiency electron-mediated processes, e.g. charge-transfer photodissociation (CT/PDIS). Such processes, however, result in the creation of fragments with a wide range of energies. This is less than ideal for studies of reaction dynamics.

While insulator surfaces offer the advantage of small quenching probabilities, the rigidity of chemical, rather than physical, bonding is desirable in that it should create more constrained collision geometries. Until now the only photochemical studies of chemisorbed species have been on metals and semiconductors. However, investigations of the acid/base
characteristics of MgO(001)\textsuperscript{57,86} have suggested a third group of photochemical systems: chemisorbed adsorbates on insulators. A recent TPD and FTIR study of acetic acid/MgO(001)\textsuperscript{57} has shown that the acid dissociates on the surface heterolytically to produce acetate and H\textsuperscript{+}, with the acetate bound in a monodentate fashion by the O\textsuperscript{-} to an Mg\textsuperscript{2+} surface cation. In the gas phase, CH\textsubscript{3}CO\textsubscript{2}H predissociates at 193 nm to form OH and CH\textsubscript{3}CO, the latter of which is born with enough internal motion to dissociate further to CH\textsubscript{3}+CO. The energy levels of a bound acetate ion on a single crystal surface, however, should be highly perturbed from those of the acid. Modified photodissociation dynamics should be expected; for example, a shift in the absorption maximum or a change in the absorption cross-section might occur. Even the question of which bond should break first in the dissociation event, C-CH\textsubscript{3} or C-OMg, is not easily answered.

A variety of systems can be imagined in which chemical binding of adsorbates through acid-base interactions might occur. Basic oxides such as MgO, amphoteric oxides like Al\textsubscript{2}O\textsubscript{3}, and even acidic oxides such as SiO\textsubscript{2} suggest themselves as possible substrates. Possible adsorbates for study can be found among the oxo-acids; e.g., the carboxylic acids, nitric acid, and sulphuric acid.
Thesis Summary

Results of thermal desorption and photodissociation studies of CH₃Br adsorbed on LiF(001), NaCl(001), and MgO(001) are presented. Translational energy distributions (P(Eₜ')) and angular distributions (P(Θ')) of the methyl photofragments gave structural information of the CH₃Br adlayers. In the cases of CH₃Br/LiF(001) and CH₃Br/MgO(001) the energy and angular distributions also suggested the involvement of a reactive pathway, the exchange reaction:

\[ \text{CH}_3 + \text{BrCH}_3(\text{ad}) \rightarrow \text{CH}_3\text{Br} + \text{CH}_3' \]  
(1)

Characteristic thermal desorption behaviour was observed for CH₃Br(ad) on LiF(001), NaCl(001), and MgO(001). Only one peak was observed in the TPD of CH₃Br/LiF(001), with a desorption energy (E_d) that decreased from 0.35 to 0.26 eV between 0.03 and 0.3 ML (monolayers), indicating repulsive adsorbate interactions. These repulsive interactions likely resulted in CH₃Br 'wetting' the surface, at least at low coverages. On NaCl(001) and MgO(001), both monolayer and multilayer peaks were observed. In the case of CH₃Br/NaCl(001), the desorption energy of the monolayer peak increased slightly with energy, while for CH₃Br/MgO(001) the monolayer E_d decreased, indicating repulsions as for CH₃Br/LiF(001). The repulsive interactions indicated for the LiF and MgO cases were likely due to the small unit mesh parameters of the two substrates, which caused crowding of the molecules. Methyl bromide was more easily accommodated on NaCl. The average E_d of the monolayer and multilayer peaks for NaCl were 0.38 and 0.33 eV, and for MgO, 0.33 and 0.28 eV. Additionally, a metastable adsorption state with E_d=0.26 eV was observed for MgO(001).
Two photochemical pathways for production of methyl radicals are reported in this thesis. These are termed 'direct' (DIR) and 'indirect' (IND). In the cases of CH₃Br/NaCl(001) and CH₃Br/MgO(001) two IND peaks, IND(1) and IND(2) were observed. The DIR methyl photofragments had P(E_T') similar to the gas phase, indicating that the DIR methyls did not undergo collisions while escaping the adlayer. The IND methyls had mean translational energies ~1 eV lower than the DIR, indicating collisional energy loss. Despite such strong collisions, the widths of the peaks in the IND P(E_T') were not greatly broadened from those of DIR. This suggested that the decrease in the translational energy of the IND methyls was likely due to a single collision with a restricted range of collision geometries. The collision geometry was probably restricted by the surface alignment. A summary of the peak energies and approximate FWHM of the DIR and IND peaks are presented in table 1.

Because the DIR methyls escaped without collisions, they retained the directionality of the prior Br-C bond. The DIR P(θ') therefore is a reflection of the distribution of angles between the Br-C axis and the surface normal. For all the systems studied, the DIR P(θ') was found to be peaked off normal, indicating that the CH₃Br molecules producing DIR CH₃ were tilted away from the normal, in much the same way that the molecules of the β-phase CH₃Br crystal are tilted 25° from the c crystal axis. The peaks in the DIR angular distributions for low and high coverage on all three substrates are summarised in table 2.

As table 2 indicates, the widths of the CH₃Br/MgO IND(1) translational energy distributions were approximately the same as those for DIR from the same substrate, despite the loss of 1.1 eV of translation in a strong collision. Additionally, the peaks in the DIR angular distributions were remarkably
<table>
<thead>
<tr>
<th>Substrate</th>
<th>DIR H.C.</th>
<th>DIR L.C.</th>
<th>IND(1) H.C.</th>
<th>IND(1) L.C.</th>
<th>IND(2) H.C.</th>
<th>IND(2) L.C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF(001)</td>
<td>2.4 (0.6)</td>
<td>2.3 (0.8)</td>
<td>9.0 (1.0)</td>
<td>0.9 (1.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl(001)</td>
<td>2.4 (0.7)</td>
<td>2.4</td>
<td>1.1</td>
<td>1.1</td>
<td>0.5*</td>
<td>0.5</td>
</tr>
<tr>
<td>MgO(001)</td>
<td>2.3 (0.6)</td>
<td>2.3 (0.6)</td>
<td>1.1 (0.5)</td>
<td>1.1 (0.5)</td>
<td>0.6 (0.9)</td>
<td>0.6 (1.0)</td>
</tr>
</tbody>
</table>

Table 1: Peak energies (eV) of translational energy distributions for the DIR and IND pathways of methyl formation. FWHM (eV) of the peaks are included in parentheses for the cases for which it could be ascertained. Only one IND channel from CH₃Br/LiF was observed; its peak and FWHM are reported in the IND(1) column. H.C. = high coverage (13 ML for LiF and NaCl, 10 ML for MgO); L.C. = low coverage (1 ML); *At this coverage the peak was very small.
Table 2: Peaks and FWHM of methyl angular distributions for the DIR, IND(1) and IND(2) pathways. Data presented are measured angular distributions (i.e. not corrected for tilt angle) except LiF(100) H.C. L.C and H.C. as per Table 1. Note that IND(1) and IND(2) could not be separated for NaCl(001), so only the total IND angular distribution is reported in the IND(2) columns.
similar to those of IND(1) from the same substrate (table 2). The former suggests a constrained collision geometry, while the latter implies that the IND(1) methyls, like DIR, retained the prior Br-C bond direction. The loss of such a significant fraction of the initial translational energy could only have been due to a low impact-parameter collision. Such dynamics are consistent with the exchange reaction (1) above. The slight peak in the IND pathway of multilayer CH$_3$Br/LiF(001) near 25° suggests that reaction (1) might also be operative in that system.

The P(Θ') of the IND methyls of CH$_3$Br/LiF (notwithstanding the small peak ca. 25° at high coverage) and CH$_3$Br/NaCl, and the IND(2) methyls of MgO, were predominantly broad, and peaked at Θ'=0. The IND pathway was the major channel at low coverage (<2 ML) on LiF (DIR/IND = 0.2) suggested that the majority of CH$_3$Br lay down (Br-C axes nearly parallel to the surface) at this coverage, standing up (Br-C axes 20° from the normal) to give primarily DIR methyls at higher coverages. This change in configuration accords with results obtained by polarised Fourier transform infrared spectroscopy (FTIR) by other workers in this laboratory. The predominance of IND methyls at all coverages on NaCl and MgO suggested that the Br-C axes of CH$_3$Br predominantly lay down at all coverages. In the case of NaCl, this was also confirmed by polarised FTIR.
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