

State-specific Reaction Dynamics

by

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Declaration

This thesis is of my own composition and is based on work carried out whilst a member of the molecular beam laser spectroscopy group in the Chemistry Department at the University of Edinburgh.

Signed :

Date : 14/12/94

To all my family.

“Is there any point to which you would wish to draw my attention ?”

“To the curious incident of the dog in the night-time”.

“The dog did nothing in the night-time”.

“That was the curious incident, remarked Sherlock Holmes.”

-A.C. Doyle, *Memoirs of Sherlock Holmes* (1893)

Abstract

The aim of this thesis was the experimental investigation of fundamental, gas phase, bimolecular chemical processes, using laser methods for the state-selective preparation of reagents and for the state-specific detection of nascent products.

An apparatus was developed which allowed the state-specific spectroscopic detection of gas phase molecules by either laser-induced fluorescence (LIF) or resonance-enhanced- multiphoton-ionisation (REMPI). The apparatus incorporates time-of-flight (TOF) mass discrimination of ions produced in the REMPI process.

A spectroscopic investigation was performed to establish whether LIF or REMPI was the optimum detection method for the OH radical. Our preliminary conclusion was that LIF remained the optimum method for the detection of OH.

The dynamics of elementary $O(^3P)$ atom + saturated hydrocarbon reactions have been investigated experimentally. Reaction was initiated by pulsed laser photolysis of NO_2 precursor molecules to produce reactive $O(^3P)$ atoms with a characteristic distribution of recoil velocities. These atoms collide and react with saturated hydrocarbon molecules chosen to contain representative primary, secondary and tertiary C-H bonds, respectively. The nascent $OH(X^2\Pi)$ product was detected in a state-specific fashion by LIF. The partitioning of the available energy among vibrational, rotational and fine-structure states of the products has been determined.

The (2+1) REMPI spectroscopy of HCl was investigated to determine which transitions would be suitable for the measurement of ground state rovibrational populations of nascent HCl produced in a chemical process. Certain vibronic bands of the $V^1\Sigma^+ \leftarrow X^1\Sigma^+$ transition were found to be sufficiently unperturbed to be suitable candidates for population studies.

These spectroscopic methods have been applied successfully to the observation of non-equilibrium populations of molecules. Vibrationally excited, but rotation-

ally relaxed, HCl was detected as a product of the reaction $\text{H} + \text{Cl}_2$, in an experiment in which H atoms were generated by microwave discharge in molecular H_2 .

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Chapter 1

Introduction

1.1 Preamble

The field of chemical reaction dynamics is concerned with the intimate details of chemically reactive events. The aim is to determine the motions of individual atoms or groups during the critical transition between reagents and products as old chemical bonds are broken and new ones formed and ultimately to explain this behaviour in terms of the chemical forces acting between fragments. In practice, these motions are generally not observed directly but are inferred by extrapolation from those of the asymptotically separated products or from the effects of the motions of the reagents on the outcome of the encounter.

Both theoretical and experimental approaches to chemical reaction dynamics are aimed at investigating key microscopic properties of a chemical reaction, some of which are:

1. to classify the type of reactive encounter
2. to estimate the reactive cross section
3. to investigate the roles of translational, vibrational and rotational energies on the outcome of a chemical reaction
4. to study how steric effects can affect the outcome of a chemical reaction.

1.2 Theoretical Approaches to Reaction Dynamics

The aim of theoretical reaction dynamics is to predict the outcome of reactive molecular collisions. Comparison of theoretical and experimental results allows the refinement of the governing potential energy surface (PES) and ultimately determines our understanding of reactive collisions.

Most theoretical approaches basically consist of solving the equations of motion for a particular system of particles, under the influence of a given potential energy function and for a particular set of initial conditions.

The PES's can be generated via semi-empirical methods[1] or full ab initio calculations. In practice, semi-empirical surfaces tend to be used more often since they allow the PES to be systematically varied until the measured dynamics of a particular system are accurately simulated. Ab initio calculations can only provide the main topographical features of a surface and presently are limited to systems with only a few electrons.

The equations of motion can be derived from a classical, quantum or semi-classical basis.

1.2.1 Classical Methods

The classical approach involves solving Hamilton's equations of motion[2][3][4] where the position and momentum of the constituent particles are absolutely defined quantities. For each set of initial conditions the time development of the coordinates of each particle in the centre-of-mass frame is computed. This is called a trajectory.

The classical trajectory method is relatively simple and therefore computationally non-intensive (cheap!). It allows a good physical insight into the dynamics of reactive collisions. The agreement with experiment can be good[5] and discrepancies can usually be blamed on the PES. The main limitations of the method

are that quantum effects are either approximated (since continuous variables are used) or completely neglected (e.g. tunneling).

1.2.2 Quantum Mechanical Methods

In quantum mechanical scattering calculations the absolutely defined position and momentum coordinates are redefined in terms of probability wavefunctions. The wavefunction is the product of a spatial distribution function and a phase factor which describes the time dependence of the wavefunction. The wavefunction is commonly referred to as a “wavepacket”.

The quantum mechanical analogy of solving Hamilton’s equations in classical mechanics is to solve the time- dependent Schrodinger equation. This approach is not frequently used in practice due to the computational difficulties associated with such calculations.

If the time for the wavepacket to spread is substantially greater than the duration of a collision then the time dependence can be neglected. The availability of large memory vector computers has permitted the development of the exact solution to the time independent quantum dynamics of small molecular systems[6]. Much effort has been devoted in the past few years to the $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ reaction[7], [8], [9] and it’s isotopic variants[10], [11]. These reactions remain the only systems for which fully converged, three dimensional, quantum mechanical scattering calculations have been performed on a “chemically accurate” *ab initio* PES. Recently, the $\text{F} + \text{H}_2 \rightarrow \text{FH} + \text{H}$ reaction has also been studied by time-independent quantum dynamical methods [12] with sufficiently accurate data to complement experiment.

However, although possible for relatively simple systems the solution of the time-independent Schrodinger equation is still far from trivial which has led to the need for semi-classical methods for studying molecular collisions.

1.2.3 Semi-Classical Methods

Quantum mechanical probabilities show the characteristics of interference; these are oscillations in the probability which arise from cross terms when the wavefunction is squared. In classical mechanics the probabilities are calculated directly from trajectories. To get interference from classical mechanics one would have to take the square root of the probability, but without further information this is undefined to within a phase factor ϕ , for we note that

$$P = (P^{1/2} \exp i\phi)^2 \quad (1.1)$$

Semi-classical mechanics provides a recipe for assigning a phase ϕ to a classical trajectory. The origins of this lie in the old quantum theory of atoms developed by Bohr. His recipe for quantisation can be written

$$\oint pdq = nh \quad (1.2)$$

where n is an integer, p and q are the momenta and position coordinates, h is Planck's constant and the integral, called the action integral, is taken over a complete orbit. In semi-classical mechanics the phase associated with a classical trajectory is calculated by the formula

$$\phi = \hbar^{-1} \int_i^f pdq \quad (1.3)$$

Semi-classical calculations are intermediate in difficulty between classical and totally quantum mechanical calculations. In the results one can distinguish between collisions leading to classically allowed transitions and those with small transition probabilities which are classically forbidden. Semi-classical calculations are particularly needed for systems where the number of classical trajectories leading to a particular final result is zero or at least very small.

1.3 Experimental Approaches to Reaction Dynamics

There are basically two main experimental approaches to chemical reaction dynamics: these are molecular beam scattering methods and spectroscopic based methods, respectively. Together these techniques have shifted the focus of much of modern physical chemistry from macroscopic kinetics and thermodynamics to the physics of chemical reactions at a molecular level.

1.3.1 Molecular Beam Scattering Methods

In a molecular beam scattering experiment the reactant molecules (or atoms) are formed into collimated beams (preferably with narrow velocity distributions and typically from a supersonic nozzle beam source). The beams are then allowed to intersect (usually at right angles) in a small region in which the scattering occurs. The ambient pressure is kept low say, 10^{-6} Torr to minimise secondary collisions. A discriminating detector, for example an electron bombardment mass spectrometer, can be rotated at various angles with respect to the beam system and thus measure the angular distribution of the various scattered species in the laboratory coordinate system. At the same time their speed distributions can be measured using time-of-flight methods. From the laboratory angular and speed distributions of one or more of the scattered products, the detailed differential cross section in the centre-of-mass system can be evaluated. The collision energy can be varied by using different seeding ratios within the supersonic beam. Atomic or molecular beams can be oriented by using strong magnetic or electric fields[13]. Although conventional detectors measure the total flux of a given product they are unable to determine internal state distributions directly, these can only be inferred through energy conservation with poor resolution.

1.3.2 Spectroscopic Based Methods

In contrast, in spectroscopic experiments high resolution spectroscopic detection methods are used to measure directly the product internal state distributions resulting from bimolecular reactions.

One of the earliest spectroscopic techniques for obtaining information regarding the energy distributions in the products of simple reactions was the “arrested relaxation” method[14]. This technique detected the infrared chemiluminescence from a chemical reaction, from which the product state rovibrational distributions could be deduced. Experiments were performed at low pressures, typically 10^{-6} Torr, where the mean free path of the molecules was of the same order of magnitude as the dimensions of the reaction vessel. The walls of the reaction vessel were cooled by liquid nitrogen, so that excited product state molecules were adsorbed sufficiently strongly for their energy to be removed completely. This meant that they could not collide further within the reaction region. There were sufficient collisions in the zone where the two streams of reagent gases crossed to equilibrate the translational energy and therefore to ensure that product molecules in different rovibrational states (and thus with different translational energies) take the same time, on average, to reach the walls. As a result the measured rovibrational distributions correspond very nearly to the relative rates at which the reaction populated the levels.

Modern spectroscopic methods used to investigate the dynamics of bimolecular reactions rely heavily on the use of laser based detection which offers much higher quantum state detection sensitivity and resolution. The laser spectroscopic detection methods used in this work were Resonance Enhanced Multiphoton Ionisation (REMPI) and Laser-Induced Fluorescence (LIF).

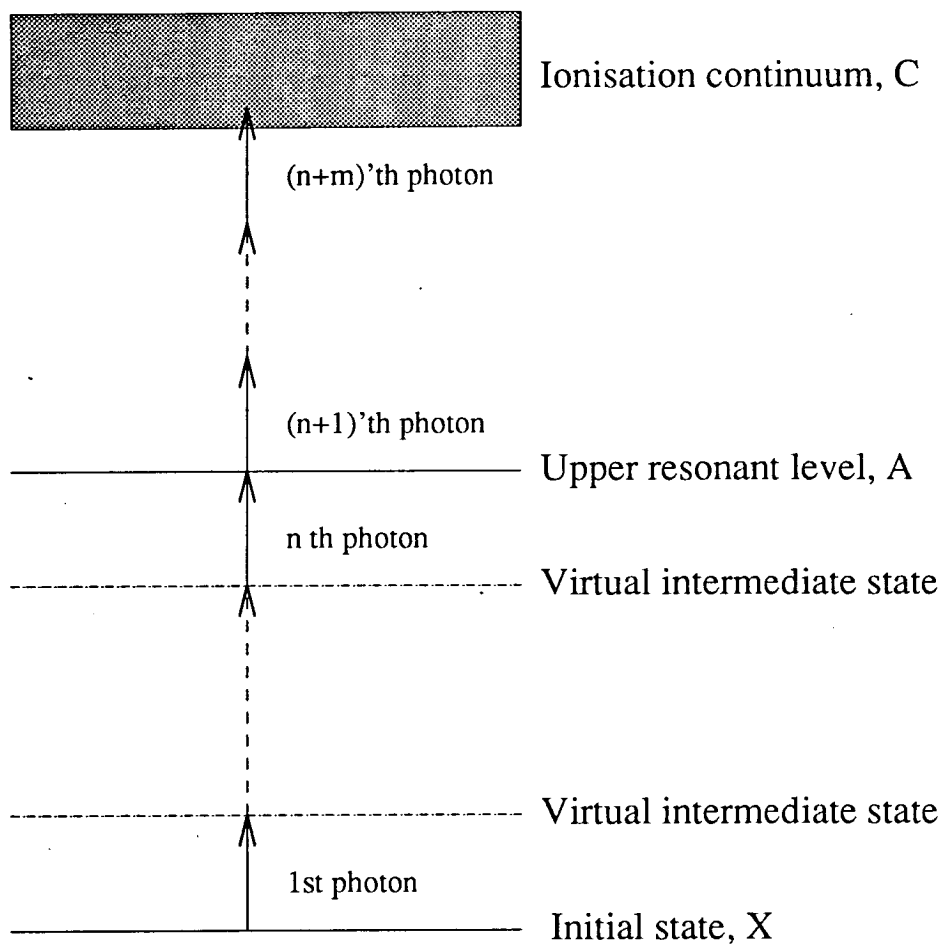


Figure 1-1: Schematic of the REMPI process

1.4 REMPI Detection

Figure 1-1 demonstrates the principles of the REMPI process. The molecule in electronic state X undergoes simultaneous absorption of n photons to reach the resonant intermediate electronic state A . Absorption of a further m photons takes the molecule into the ionisation continuum C . The $n + m$ photons may come from either a single laser beam passing through the absorbing sample or they may come from two or more beams emitted from one or several lasers.

The simplest and most common REMPI experiment consists of a tunable dye laser focused into a low pressure gas. Electrons or ions created by the laser pulse are collected, the current is amplified and the resultant signals recorded as a function of laser wavelength.

There are several advantages of using such an $n + m$ process:

1. spectra of these multiphoton transitions often display quite different information from a single- photon experiment because of altered selection rules and transition probabilities.
2. the use of polarisation measurements make it possible to identify state symmetries by simple empirical means[15].
3. simple species often have their first excited states lying in the UV or VUV. Studies using two or more photons of visible or UV radiation are much easier to perform than using single- photon VUV radiation.
4. when the correct combination of photons with resultant momentum equal to zero is used, the resulting spectra are free from Doppler broadening.

The first and third advantages listed are most applicable to this work, where the main aim was to extract ground state product populations from bimolecular reactions.

Typical cross-sections for a multiphoton process are $10^{-50}\text{cm}^4\text{s}$ for a two photon absorption and $10^{-82}\text{cm}^6\text{s}^2$ for a three photon transition[16]. From these small

numbers it is apparent that very high light fluxes are needed to achieve a significant transition probability. Typical modern pulsed dye lasers have powers of around 10^5 Watts in 10^{-8} second pulses and are the only real choice as light sources.

Rate equations can be written to describe the kinetics of such an $n + m$ absorption process[16].

$$dX/dt = -\alpha X + (\alpha + \gamma)A \quad (1.4)$$

$$dA/dt = \alpha X - (\alpha + \beta + \delta + \gamma)A \quad (1.5)$$

$$dC/dt = \beta A \quad (1.6)$$

where X, A and C are the respective populations of molecules in the ground electronic state, the resonant electronic state and the ionisation continuum, $\alpha = \sigma_1 I^n$, $\beta = \sigma_2 I^m$, where σ_1 and σ_2 are cross sections, I is the laser intensity, γ is the fluorescence rate and δ is the radiationless transition rate to a species that does not ionise.

The solution to these equations for a square pulse excitation is

$$C = \frac{\beta X_0}{\beta + \delta} \left(1 + \frac{L e^{-Kt}}{K - L} - \frac{K e^{-Lt}}{K - L} \right) \quad (1.7)$$

where

$$Y = 2\alpha + \beta + \gamma + \delta \quad (1.8)$$

$$Z = \gamma + \beta \quad (1.9)$$

$$K = Y/2 + 1/2(Y^2 - 4\alpha Z)^{1/2} \quad (1.10)$$

$$L = Y/2 - 1/2(Y^2 - 4\alpha Z)^{1/2} \quad (1.11)$$

At moderate intensities under the normal situation where $\beta \gg \alpha$, the ionisation step is kinetically saturated and the overall probability is proportional to $\sigma_1 I^n$. Therefore the spectrum recorded as a function of laser wavelength is appropriate only to the A-X transition. This fact underlies the usefulness of REMPI as a method for recording multiphoton spectra from which X state populations can be deduced.

1.4.1 Line Broadening Effects

The focused high laser intensities used in REMPI or LIF experiments can cause saturation effects which can drastically affect the resolution of a spectrum.

In REMPI experiments saturation line broadening arises due to the fact that the excitation and ionisation processes must take place within the duration of a single laser pulse. For a 5 ns pulse the uncertainty principle limits the linewidth to a minimum of 200 MHz. It is usually the case, however that the ionisation step is much more probable than the excitation step so that when reasonable signal levels are achieved the excited state lifetime is considerably shortened and thus the energy of the state effectively broadened. For an $n + m$ process the degree of lifetime broadening is a function of n/m , thus the broadening for a 3+1 process would be greater than for a 2+1 process. Similarly in LIF experiments lines can be power broadened resulting from reduced excited state lifetimes due to rapid optical pumping rates at high laser intensities.

Another cause of line broadening is the quadratic AC Stark effect[18] [19][20]. The degree of broadening can be quite extensive even at moderate laser powers, about $2\text{cm}^{-1}/\text{GWcm}^{-2}$. The effect is so-called because the energy level shift (Stark shift) depends quadratically on the electric field strength. The AC stark shift depends purely on the laser intensity and hence arises from both temporal and spatial effects within the laser pulse. However, a normal experimental configuration (conically focused beam) is such that spatial effects dominate.

Consider two identical species at positions A and B within the focused beam where the intensity at A is greater than at B. The quadratic AC Stark shift predicts that the shift in the resonance frequency is proportional to the radiation intensity. Therefore, the line shift at A will be greater than at B. The process results in a broadening of the transition. In the presence of an AC Stark effect the effective order of the non-linear dependence on intensity for a multiphoton process may differ considerably from that predicted.

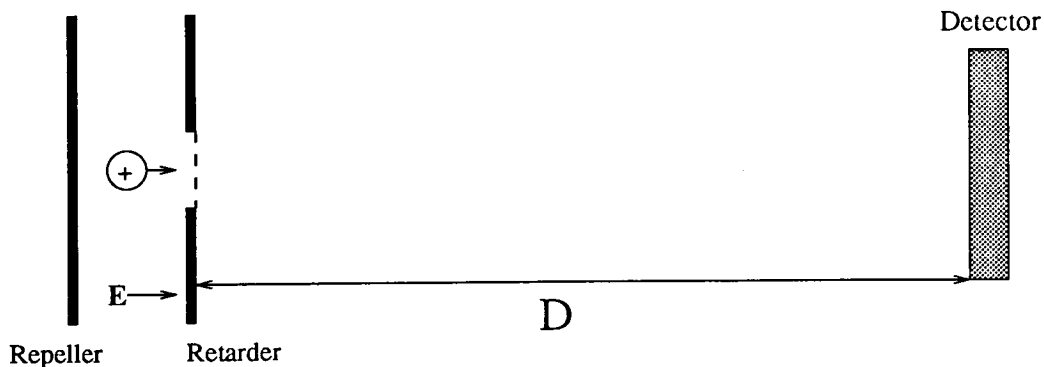


Figure 1-2: Schematic of a single field linear time- of-flight mass spectrometer

1.5 REMPI-TOF/MS

An added feature of our apparatus was the use of a linear time-of-flight mass spectrometer (TOF/MS), which enabled different ion masses to be resolved.

A simplified schematic of a single field linear TOF instrument is shown in figure 1-2. Ions, created via a laser pulse, are accelerated through a fixed potential entering a field free drift tube. All the ions are extracted, to a first approximation, with the same kinetic energy, so that ions of different masses travel at different velocities through the drift tube, thereby separating in time before reaching the ion detector. The flight time, (t), depends on the ion mass, (m), according to

$$t = Km^{1/2} \quad (1.12)$$

where K is a proportionality constant, determined by the particular design parameters of the instrument.

The lighter, faster moving ions reach the detector before the heavy, slower ions. By recording the ion intensity as a function of time, a time-of-flight spectrum is generated.

1.5.1 Resolution in a TOF/MS

The mass resolving power of a TOF/MS is defined as

$$R = \frac{m}{\Delta m} = \frac{t}{2\Delta t} \quad (1.13)$$

where Δm is the FWHM spread in ion mass and Δt is the temporal width of the ion packet.

Schlag[22] introduced an alternative definition of mass resolution,

$$R = \frac{m(t_2 - t_1)}{\Delta t} \quad (1.14)$$

where $(t_2 - t_1)$ is the time-of-flight difference for two neighbouring mass peaks of mass m and $(m + 1)$ and Δt is the temporal width of the ion packets.

As mentioned previously, flight times are given by $Km^{1/2}$, so that the difference in flight times between successive peaks decreases as mass increases. At high masses, therefore, the resolving power of the instrument is degraded and eventually, when the FWHM of the individual ion packets is equal to the temporal difference between neighbouring peaks, it will not be possible to resolve ions separated by 1 amu. The conditions at which this is reached depends on the widths of the ion packets and the value of K . The temporal width of an individual ion packet is limited by a number of broadening mechanisms, which are discussed below.

1.5.2 Spatial Resolution

Since it is impossible to focus a laser beam down to a single point, ions are created over a finite spatial volume. If two ions of the same mass/charge ratio and initial kinetic energy are created at the same time, but at different positions along the spectrometer axis, they will be extracted from the source with different kinetic energies. The difference in time of flight due to formation of ions over a range of positions and therefore potentials, within the ion source, broadens the ion temporal profiles. This effect is known as the spatial resolution of the mass spectrometer and can be overcome to a large extent by employing the double-field linear TOFMS design of Wiley and McLaren (see reference (1) of chapter 2).

1.5.3 Energy Resolution

A distribution of initial ion kinetic energies, caused by the distribution of kinetic energies for the initial neutral molecules, results in ion packets of finite temporal width. The limiting resolution due to this effect is known as energy resolution.

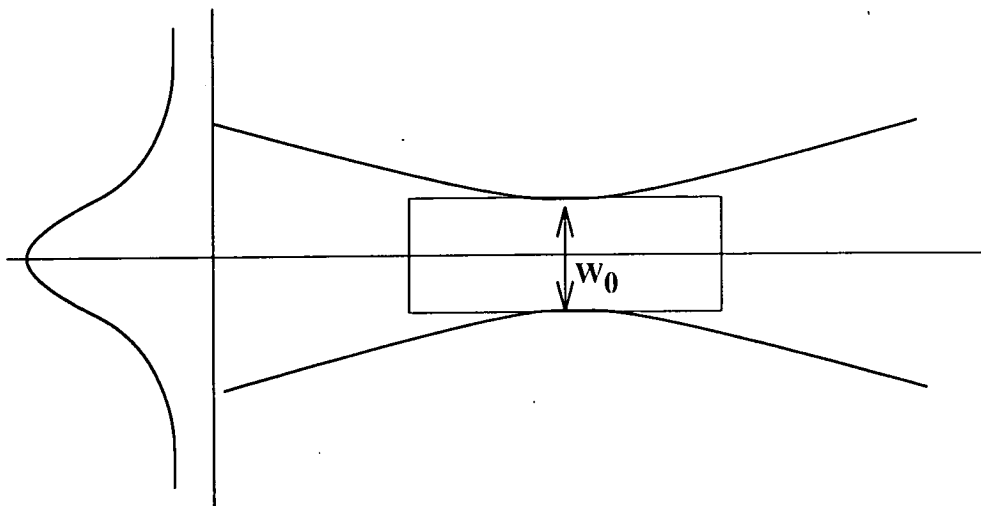


Figure 1-3: Schematic illustrating the focusing process. The bell shaped curve is the Gaussian beam profile. w_0 is the waist diameter of the focused laser beam. The rectangular box indicates the cylindrically symmetric focal region.

1.5.4 Timing Resolution

In a simple TOF/MS, it is not possible to produce ion packets which have temporal widths less than that of the laser pulse width. This limiting resolution due to this effect is known as timing resolution.

1.5.5 Space Charge Effects

The width of an ion packet can be broadened due to electrostatic repulsion between ions. It has been estimated that these effects become significant at ion number densities of 10^7 - 10^8 cm^{-3} [23].

1.5.6 Laser Intensity Effects

Figure 1-3 illustrates the focusing process for a Gaussian beam profile. For the Rayleigh length the focus region has approximately cylindrical symmetry, however away from that, the conical geometry of the beam creates a rapid intensity variation and the intensity drops off in proportion to the square of the distance from the focus. It is often quite easy to saturate the ionisation in the focus region. When this happens, continuing to increase the laser intensity creates no

more signal within the Rayleigh length, but the ionisation region begins to move out into the conical focus regions. In this case it can be shown that the power dependence goes as $I^{3/2}$, irrespective of the number of photons involved in the ionisation step[17].

The exact dependence of the MPI signal on the laser intensity can be found using the method described by Bernstein et. al. [21]. They found that for a spherical lens, for any fixed laser power, the MPI intensity is proportional to f^{4-2n} . Thus, it is possible to determine the power law index from the slope of a log-log plot of the ion signal versus focal length.

1.6 LIF Detection

The use of LIF for determining the relative populations of individual quantum states was first realised in two papers by Zare[24][25], that demonstrated the utility of such measurements for investigation of single chemical reactions and for molecular beam diagnostics.

The basic idea of LIF is simple. Light from a tunable laser is impinged on the sample to be investigated. As the frequency of the laser is changed, molecules within the irradiated portion of the sample will be excited to fluorescence whenever the spectral envelope of the laser overlaps an absorption line of the molecule. The fluorescence emitted is normally collected at right angles to the direction of the excitation laser beam propagation. Since the only molecules excited are those in the specific lower level(s) of the corresponding transition, the excitation is selective for this state or group of states. Hence, the excitation spectrum obtained by recording the fluorescence intensity as a function of wavelength reflects the relative populations of these different states.

LIF has been successfully applied with both linear [22] and non-linear[23] excitation processes, in both atomic and molecular systems. The description given here is of more relevance to the linear regime, being in accord with the study of the OH radical in chapters 3 and 4. However, the arguments presented can normally be extended to non-linear excitation without loss of generality.

Altkorn and Zare[28] derived a general expression for the detected fluorescence intensity assuming that all states being studied have the same lifetime and quantum yield for fluorescence and that the LIF process can be accurately modelled using a two level system (ground and excited electronic states).

The result obtained for the detected fluorescence, I , is

$$I = K \int \frac{n(\theta)a_{21}b_{12}\rho}{2b_{12}\rho + A_{21}} \times \{1 - \exp[-(2b_{12}\rho + A_{21})\Delta t_L]\} d\Omega \quad (1.15)$$

where

K is a constant depending on the details of the detection system.

Δt_L is the laser pulse duration.

a_{21} and b_{12} are *directional* Einstein coefficients and A_{21} is an *integrated* Einstein coefficient. Integrated Einstein coefficients are quantities averaged over light of all directions and two orthogonal polarisations, as well as molecules of all orientations. In LIF experiments we are concerned with directional radiation and molecular distributions that are often anisotropic. In order to treat the LIF process, it is convenient to introduce the directional Einstein coefficients which are used to model the interaction of polarised radiation with molecules having a specific orientation.

ρ is the laser radiation density.

$d\Omega$ is the solid angle into which light is collected.

$n(\theta)$ is the molecular distribution, where θ is the angle between the $\mathbf{J}$ vector of the molecule and the axis of cylindrical symmetry (defined as the axis mutually orthogonal to the probe laser direction and to the axis of fluorescence detection) and is commonly expressed through an expansion in Legendre polynomials:

$$n(\theta) = n \sum_{l=0}^{\infty} a_{2l} P_{2l}(\cos \theta) \quad (1.16)$$

where,

n is the total concentration of molecules in the state of interest.

a_{2l} are the moments of the distribution (assuming linearly polarised probe radiation and therefore only even moments)

P_{2l} are the Legendre polynomials.

Equation (1.15) can be simplified if the following 4 conditions are satisfied:

1. The pumping rate is low (i.e. no saturation)
2. The polarisation of the laser and the detected fluorescence are unchanged during the experiment.
3. The distributions of molecules in all states probed by the laser are characterised by the same values of a_2 and a_4 .
4. The fractions of collected fluorescence due to the Q branch and P or R branch transitions are the same for all states studied.

In this limit, the angular part of the integral in equation (1.15) may be incorporated into the proportionality constant to give

$$I = KnB_{12}\rho\Delta t_L \quad (1.17)$$

Equation (1.17) is the most widely used expression for extracting populations from LIF measurements. In this work, conditions 1 and 3 are generally assumed, but explicit account is taken of factors 2 and 4.

The most dramatic factor influencing the appearance of LIF spectra results from saturation effects (see line broadening discussion earlier). If present, saturation affects the interpretation of results that are based on the assumption that the observed intensity relates only to a product of linestrength and population factors. The effect is most pronounced in comparisons of states which have significantly different transition strengths since the state with the greater transition strength will saturate at much lower powers [31].

1.7 Hot Atom Dynamics Experiments

A continually developing experimental approach to the study of bimolecular reaction dynamics exploits laser photolysis of a suitable precursor molecule, AB, to produce a reactive fragment of interest, A, in the presence of a molecular reagent C.



Pulsed laser photolysis is particularly advantageous because of the transient high density of species A which can be produced effectively instantaneously. The products are probed by a state specific laser spectroscopic method, which offers far greater sensitivity and resolution than earlier spectroscopic techniques. The nascent character of the observed properties is ensured by operating with a sufficiently short time delay (determined by the pressure in the reaction chamber) between the photolysis and probe pulses.

The type of experiment just described is commonly referred to as a “hot atom” dynamics experiment. The technique has been applied widely to the study of chemical kinetics and, more recently, to reaction dynamics[30]. The work attempted in this thesis was aimed at carrying out such experiments.

Most hot atom dynamics experiments have focused on how the collision energy between the reactive fragment A and the molecular target C affects the reaction cross section or product energy disposal. Examples of such reactions include $O(^3P)+HBr$ [19], $H+D_2$ [31], $H+O_2$ [32], $H+H_2O$ [33][36], $O(^1D)+H_2O$ [34], $O(^3P)+\text{cyclohexane clusters}$ [35].

A more recent development in this field has been the study of the effects caused by internal excitation within the molecular reagent C. The molecular reagent is pumped to a desired quantum state using direct infrared excitation or non-linear stimulated Raman pumping, requiring the molecules to be irradiated simultaneously by two laser pulses with a difference frequency matched to a Raman allowed vibration-rotation transition in the molecule. Examples of such reactions include

Ca+HF($v=1, J$)[37], O(^3P)+HCl($v=2, J$) [38], D+H₂($v=1, J$) [39], H+HOD(0, 0, 1), (1, 0, 0) [41], H+D₂O(0, 0, 1), (0, 1, 1)[42].

Information on the stereodynamics of a reaction can be obtained in hot atom dynamics experiments by using polarised photolysis and probe lasers. Polarised laser photolysis of a suitable precursor generates an anisotropic spatial distribution of fragment velocity vectors, relative to the electric field vector of the photolysis beam. This anisotropy manifests itself as a directionality in the A...C collision velocities. The correlation with collision velocity vector of some other spatial property of the system, such as product rotational angular momentum or product recoil velocity, may then be measured by using a polarised probe laser. The probability of detection depends on the angle between the electric field vector of the probe laser and the molecular transition dipole. The alignment moments of the product molecules may be deduced from the variation of the intensity of the probe signal with probe laser polarisation. Also, sub-Doppler detection allows product *velocity* distributions to be deduced.

The major advantages of this technique over conventional molecular beam methods are

1. experiments can be performed with reagents which are difficult to produce in a molecular beam
2. vector correlations can be measured in a quantum state fashion.

Reactions which have had such specifically attributes examined by this method include H+O₂[43], H+simple organics[44], H+SiH₄[45], O(^3P)+CS[46], O(^3P)+HCl[47], O(^1D)+N₂O[48][49] [50], O(^1D)+CH₄[51], Cl+CH₄[52].

An obvious limitation of the technique may seem to be a degradation of the alignment of the collision velocity vectors through the thermal motions of both the photolysis precursor molecules and the reactant target molecules. In appendix A analytical expressions are derived which quantify this degradation, and for most systems so far studied the degradation in alignment is not likely to compromise seriously the viability of such experiments. Only in kinematically unfavourable, but conceivably realistic, systems will thermal velocities become a potential obstacle to polarisation measurements.

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Chapter 2

Experimental Apparatus

This chapter describes the apparatus used to carry out the hot atom dynamics experiments described in the previous chapter. The apparatus was designed to incorporate REMPI-TOF or LIF detection methods.

Details of the lasers, the vacuum system, the methods of generation of the species to be probed and the data acquisition process will be described.

2.1 Lasers

The hot atom dynamics experiments described require the use of two laser systems; one to photolytically generate an atomic precursor and the other to probe the nascent product molecules. A gas-discharge laser was used for the former of these tasks while a Nd:YAG pumped dye laser system was used for the latter.

2.1.1 Lambda Physik EMG 102E Gas-Discharge Laser

The gas-discharge laser was used as a general purpose photolysis laser. This thyatron-switched laser was operated on two different gas mixtures:

1. N_2/He to run on the N_2 line at 337 nm.
2. $\text{Xe}/5\% \text{ HCl}$ in Ar/He to run on the XeCl line at 308 nm.

The laser required a 15 V trigger pulse for external operation. A 1.4 μ s delay between the trigger pulse and the laser light output corresponded to the time taken for the high voltage capacitors to fully charge.

The high voltage discharge could be operated between 0 to 33 kV. At the maximum voltage the output energy at 337 nm was 5 mJ in a 9 ns pulse. The output energy at 308 nm at the same voltage was 50 mJ in a 9 ns pulse.

The temporal jitter of the laser pulse relative to the input trigger was measured to be 10 ns. The final output energy could be controlled by varying the high voltage discharge.

The final output beam had a rectangular cross section (40 mm $\times$ 15 mm) and was unpolarised.

2.1.2 Spectron Laser System

The Spectron laser system consisted of a Q-switched, pulsed Nd:YAG laser (SL803S), a dye laser (SL4000G), a scan controller (SL4000SC) and a wavelength extension unit (SL4000EX) which contained the appropriate doubling and mixing crystals. The combined system gave tunable laser radiation in the wavelength region 220 nm to 700 nm.

2.1.3 Spectron SL803S Nd:YAG Laser

The Nd:YAG laser consisted of an oscillator and amplifier arrangement each being pumped by its own flashlamp. The triggering of the oscillator and amplifier flashlamps, from either an internal or external source, initiated the charging of the Q-switch capacitors. When the specified flashlamp to Q-switch delay had elapsed the high voltage relay supplying the Pockel's Cell was triggered. The flashlamp to Q-switch time delay was fixed at 200 μ s. The laser was capable of delivering 800 mJ pulses of approximately 10 ns duration at its fundamental wavelength of 1064 nm. The laser was optimised for a 10 Hz repetition rate, the maintainance of which was essential due to thermal lensing effects in the Nd:YAG rods.

The fundamental harmonic (1064 nm) output was frequency doubled using a KDP crystal and the resulting second harmonic (532 nm) radiation was separated from the residual fundamental harmonic using a dichroic beamsplitter. Optimised pulse energies at 532 nm were approximately 300 mJ. The beam was horizontally polarised. The residual 1064 nm radiation was either collected into a beam dump or used for frequency mixing in the SL4000EX wavelength extension unit.

2.1.4 Spectron SL4000G Dye Laser

The Spectron SL4000G dye laser was of the oscillator/dual amplifier type. The oscillator consisted of a transversely pumped flowing dye cell, an output coupler, a diffraction grating, a wavelength tuning mirror and a prism beam expander. It was pumped by approximately 10% of the 532 nm output from the Nd:YAG laser. The grating was used in a grazing incidence configuration and wavelength tuning was achieved using a separate tuning mirror mounted on a stepper motor sine drive arrangement.

The amplifier stage consisted of two longitudinally pumped flowing dye cells. Each of the amplifiers was pumped by approximately half the remainder of the 532 nm beam. The dye circulator contained two separate reservoirs; one each for the oscillator and amplifier dye cells. Each reservoir contained approximately one litre of dye solution with the oscillator solution generally more concentrated than the amplifier solution. The final amplified dye laser beam output was horizontally polarised.

2.1.5 Spectron SL4000EX Wavelength Extension Unit

To carry out experiments in the ultraviolet region the final amplified dye laser beam output was either frequency doubled or frequency doubled and mixed with the residual Nd:YAG fundamental frequency. This gave tunable UV radiation over the wavelength region 220 nm to 350 nm.

The SL4000EX system employed parallel faced non-linear KD*P crystals for harmonic generation and sum frequency mixing, with axial effects being corrected

for by plain quartz compensating blocks. All crystals were temperature controlled to improve stability and prevent problems with water absorption. When mixing, the 1064 nm beam was directed around an optical delay line incorporating a beam diameter reducing telescope.

In order to maintain the correct phase matching conditions in the chosen doubling or mixing crystals, portions of the doubled and mixed beams were split off onto two separate photodiodes with local head amplifiers. These had adjustable gain. A dedicated BBC microcomputer monitored the respective doubled and mixed power outputs via analogue to digital convertors. As the dye wavelength was scanned the orientation of the crystals was continually updated via the BBC microcomputer to maintain optimum power output. The crystals were rotated in one angular plane by stepper motors. The drives had limit switches to detect excessive rotation of the crystals.

The doubled UV radiation typically had pulse energies of approximately 6-10 mJ, depending on the dye tuning curve and the doubling efficiency at a particular wavelength. The frequency doubled beam was vertically polarised.

The mixed UV radiation typically had pulse energies of 1-3 mJ, again depending on the dye tuning curve and the efficiency of the doubling and mixing crystals. The frequency doubled/mixed beam was horizontally polarised and had a bandwidth of $\sim 0.5 \text{ cm}^{-1}$.

Laser powers were measured using a Scientech 372 power meter or a Molectron J3-09 Pyroelectric Joulemeter.

2.1.6 Spectron SL4000SC Scan Controller

The Spectron SL4000SC scan controller was used to control the diffraction grating of the dye laser. The scan controller was connected to an IBM PC (see section 2.6.3) via one of the PC's RS-232 serial ports. This configuration enabled the dye laser to be controlled via the IBM PC.

2.2 Vacuum System

The vacuum system (supplied by Vacuum Generators UK, Ltd) could be configured for REMPI-TOF or LIF detection.

2.2.1 REMPI-TOF Detection

Figure 2-1 shows the vacuum apparatus employed in this work.

The vacuum system basically consists of two main parts; the reaction chamber and the detection chamber. All had 4" i.d. nominal sections. The reaction chamber and the flight tube were separated from the detection chamber by a pneumatic gate valve (Vacuum Generators, MGVP). This allowed the microchannel plate detector (MCP, see section 2.2.4) to be isolated from the rest of the vacuum system whenever the reaction chamber was opened to the atmosphere for modifications.

The reaction chamber was separated from the flight tube via a "top hat" flange, as shown in figure 2-1.

When neutrals were photoionised the resultant ions were accelerated through the orifice shown on the top hat flange, into the flight tube and detected at the end of the detection chamber by the microchannel plates. The orifice diameter could be changed between 2 to 10 mm. This resulted in different pressure differentials between the reaction and detection chambers. This was important for doing bimolecular experiments where it was essential to maintain high enough pressures in the reaction chamber, to ensure bimolecular collisions could occur, whilst still maintaining low enough pressures, ca. 10^{-6} mbar, in the detection chamber needed for the MCP detector. Additionally, a glass capillary array (Gallileo Corporation) with poresizes from 10 microns to 50 microns could be placed in the top hat orifice to further improve the pressure differential between the two chambers. The capillary arrays were conductively coated to prevent problems with charge building up on the channel surfaces. Up to 50 per cent of the ions are transmitted through the array.

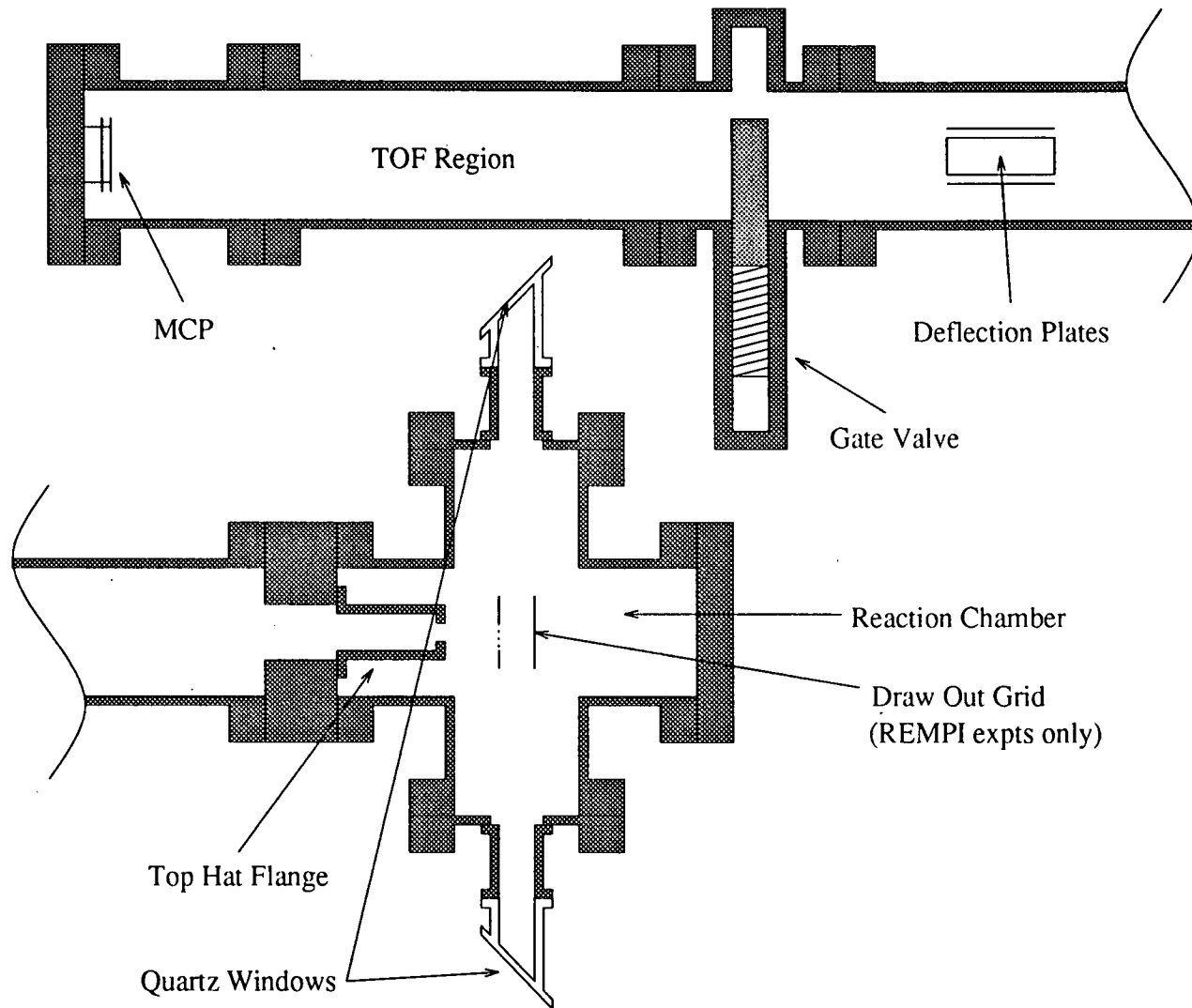


Figure 2-1: Schematic diagram of the vacuum apparatus

The reaction chamber and the detection chamber were separately evacuated by two cryotrapped 4" Edwards oil diffusion pumps (100/300M), backed by Edwards E2M8 rotary pumps, which are further protected from corrosive gases by in-line cryotrap. The flight tube was principally evacuated through the detection chamber diffusion pump although a small amount of pumping could occur from the reaction chamber diffusion pump through the top hat hole.

The pressures in the three main chambers were monitored using a system of Pirani (Edwards PR10K) and ion gauges (Vacuum Generators VIG 8) connected to a Vacuum Generators, IGC10 Series Ion gauge controller. Additionally, a MKS Baratron Type 120A capacitance manometer was used to monitor pressures too high for the reaction chamber ion gauge (i.e. pressures in the range 0.1 mTorr to 1 Torr).

Typical pressures, with no gas flowing, were 1×10^{-6} mbar in the reaction chamber and 5×10^{-8} mbar in the detection chamber, with the pneumatic gate valve open.

All vacuum seals were achieved using Viton O-rings and gaskets or copper gaskets.

2.2.2 Extraction Grids

The ions formed at the focus of the probe laser beam in the reaction chamber were extracted using a draw out grid arrangement. Figure 2-2 shows a schematic drawing of the extraction grids used.

The draw out grid consists of a repeller, a retarder and a ground plate conforming to the Wiley-McLaren[1] double field linear TOFMS design. The top hat flange acted as the ground plate.

All the ion optics were home built and were fabricated from stainless steel. The retarder had a 15 mm diameter hole cut through it's centre to transmit the ions formed after photoionisation. To eliminate any field inhomogeneities around this aperture, it was covered with nickel mesh (Buckbee-Mears, 90% transmission). Figure 2-2 illustrates how the mesh was kept in place. Tightening the screws between the two flanges shown, pulls the mesh surface even, creating a "drumskin"

- | | |
|------------------|-------------------------------|
| 1-Repeller plate | 5-Insulated connecting wire |
| 2-Retarder plate | 6-Delrin spacers |
| 3-Nickel mesh | 7-Rear flange |
| 4-O-Ring | 8-MHV Electrical feed through |

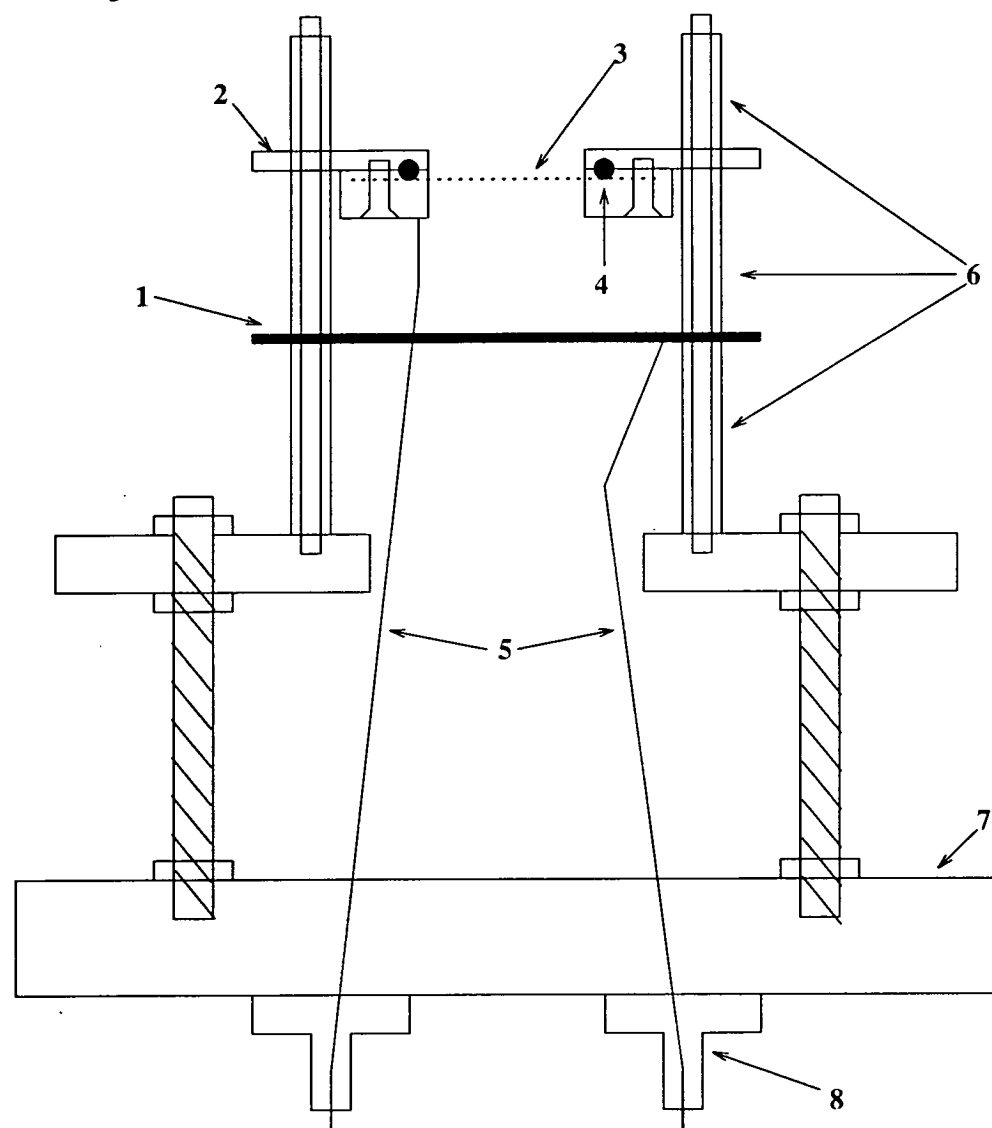


Figure 2-2: Schematic of the ion extraction grids.

effect. This was found to be the most successful method of producing an even surface for the mesh.

The repeller and retarder voltages were provided by 0-3 kV Bertran high voltage power supplies.

While the extraction optics gave perfectly good signals for simple REMPI spectroscopy experiments it was deemed necessary to alter the optics for dynamics experiments. In dynamics experiments the concentrations of nascent products to be probed is far less than in a simple spectroscopy experiment. Therefore, to extract nascent ions more quickly from the reaction chamber the retarder plate was removed and the top hat flange was repositioned so that its front face was located at the previous retarder position. An insulating spacer bolted between the flight tube and the top hat flange allowed the top hat to be electrically floated. In this configuration the top hat was acting as the retarder so that the mass spectrometer was only of the single field design. No great loss in the resolution of the spectrometer was suffered in changing from the double field to single field design.

2.2.3 Deflection Plates

Once the ions had been accelerated through the top hat hole they entered into the high vacuum, time-of-flight (TOF) region. This region contained two dimensional electrical deflection plates to allow horizontal and vertical adjustment of the ion trajectories. Figure 2-3 shows how the deflection plates were arranged. Positive or negative d.c. voltages could be applied independently to each of the deflection plates via a dual power supply (Kingshill, variable 0-150 V). A flange positioned on top of the flight tube contained the necessary electrical feedthroughs to connect the power supplies to the deflection plates.

2.2.4 Microchannel Plate Detector

The signals were detected by a dual microchannel plate (MCP) assembly[2]. The MCP (R.M. Jordan) was of a dual chevron design, with two Galileo MCP-18B

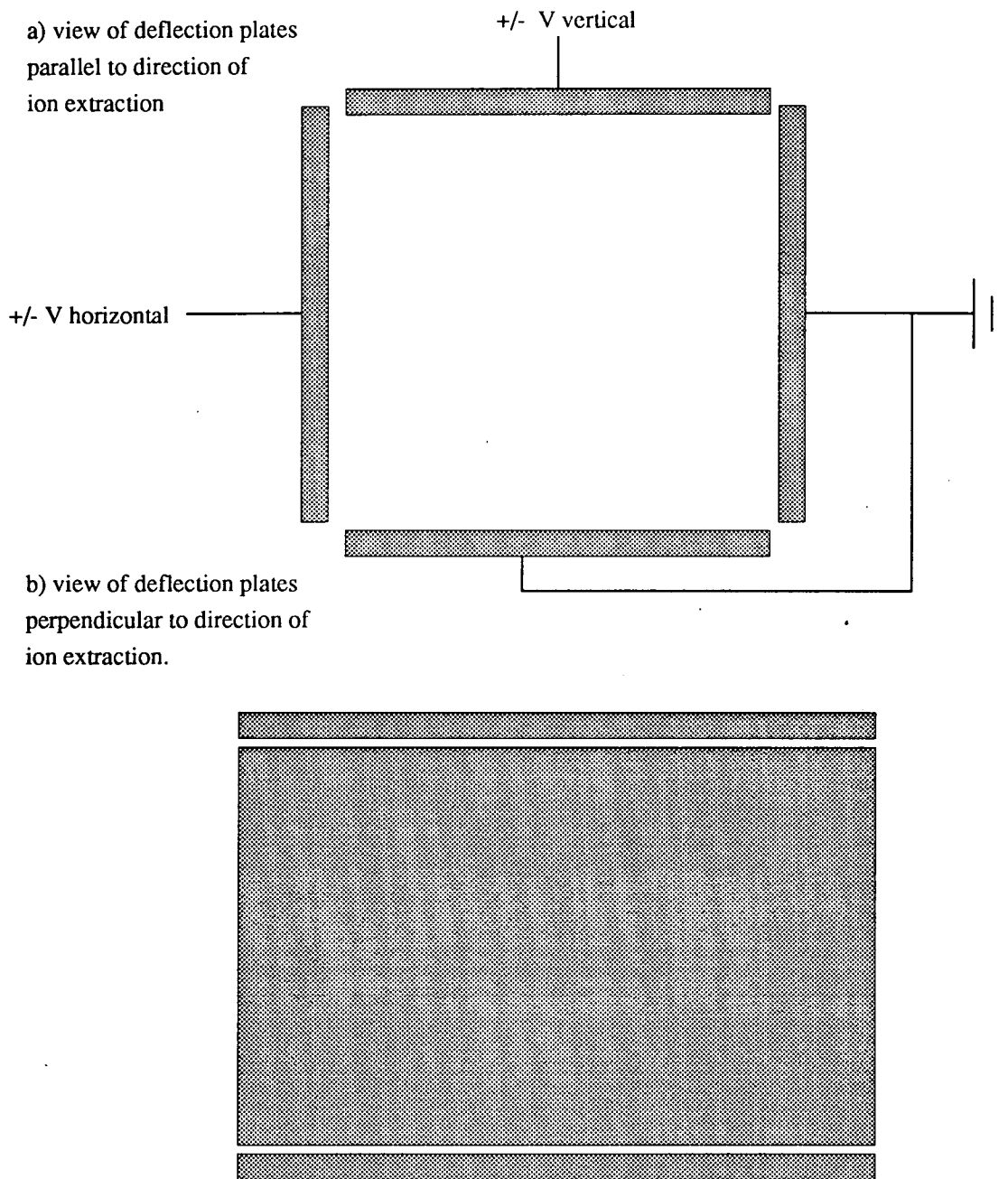


Figure 2–3: Schematic of the two dimensional electrical deflection plates.

plates back to back, each having an active area of 2.5 cm^2 . A maximum potential difference of typically 2 kV was applied between the front and rear surfaces of each plate. Additionally, an accelerating potential of approximately 1 kV was applied between the rear face of the first plate and the front surface of the second plate. In this configuration each plate had a maximum gain of approximately 10^3 resulting in a total gain of approximately 10^6 . The voltages were provided by a Bertran, 0-5 kV high voltage power supply and a voltage divider chain. The output from the MCP was amplified (Stanford Research Systems SR240), then taken into the input of a transient digitiser (section 2.6.6).

2.3 LIF Detection

A diagrammatic representation of the apparatus used in all fluorescence experiments in this thesis is shown in figure 2-4.

The flight tube and detection chamber are redundant, therefore the top hat flange was removed and replaced by a blanking flange. This isolated the reaction chamber.

In a LIF experiment the detector is situated externally to the vacuum chamber and is obviously insensitive to the pressure inside the reaction chamber. Therefore, the pressure constraints previously encountered with REMPI detection were avoided. Typical total pressures in a LIF experiment could be up to 200 mTorr.

Evacuation of the reaction chamber was through the Edwards rotary pump (E2M8) only which maintained a base pressure of 1×10^{-3} mbar.

The two main requirements for a LIF experiment are

1. an efficient light gathering and detection system
2. low levels of scattered laser light

The lens assembly shown in figure 2-4 was custom built for the experiments carried out in this work.

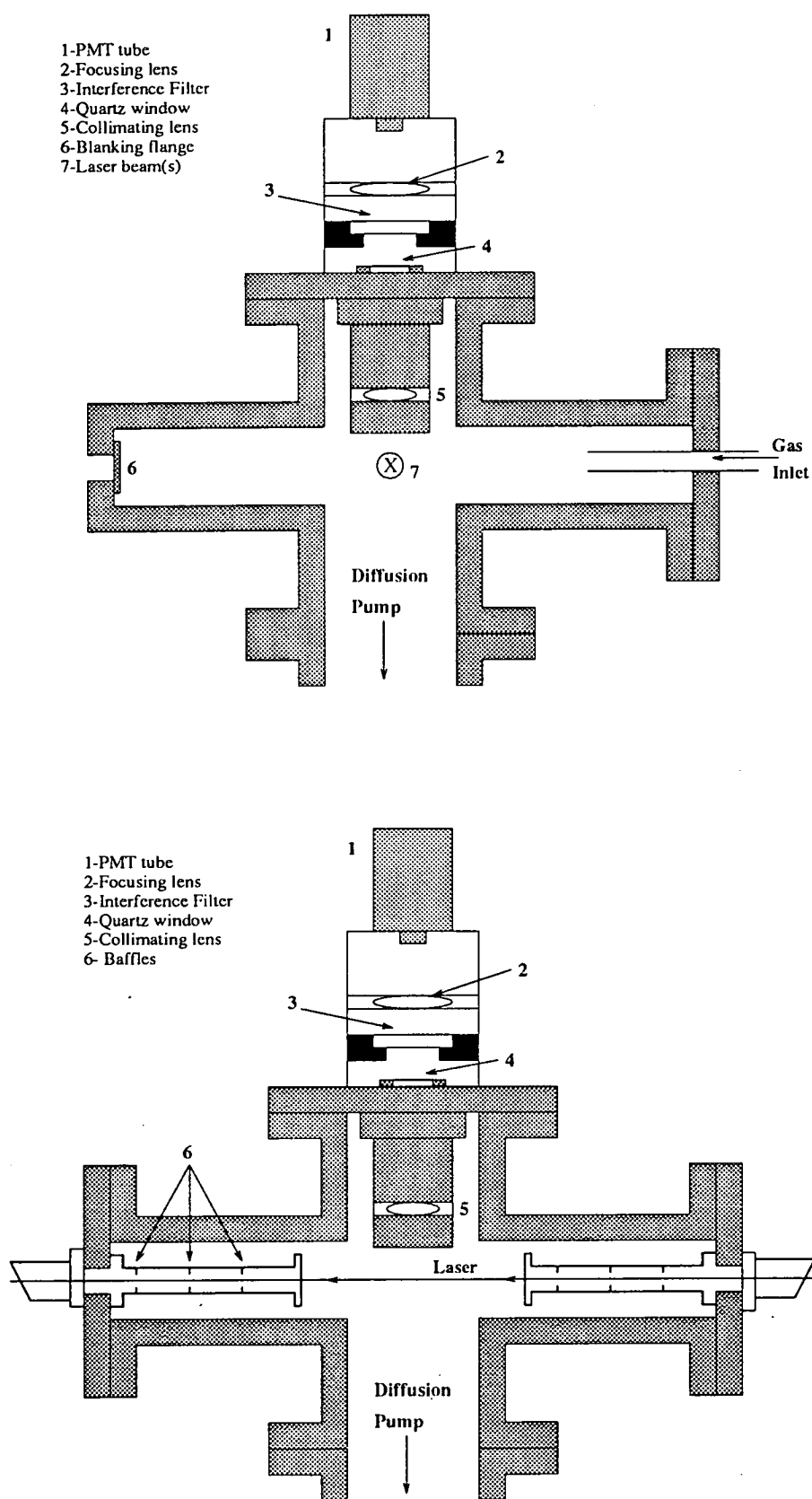


Figure 2-4: Schematic of the experimental apparatus used for LIF detection, the upper panel is a view perpendicular to the laser beam while the lower panel shows a view of the apparatus parallel to the laser beam.

Fluorescence from an isotropic sample is emitted to all solid angles. Thus, to gather as much light as possible a condensing lens with as high a relative aperture as possible was placed at a distance equal to its focal length. This first lens produced a collimated beam of light which passed through an interference filter to isolate the desired signal wavelengths. A second lens then imaged the light onto the photomultiplier tube (PMT). Both of the lenses are mounted within lens holders which could be moved vertically within the lens assembly allowing optimisation of their positions.

Several measures were taken to reduce the amount of scattered laser light potentially seen by the detector. The laser axis was defined by internally baffled entrance and exit arms (25 cm long) with fused silica windows set at Brewster's angle. The baffles were arranged so as to best trap any scattered laser light.

The lens assembly and the entrance and exit arms were painted with matt black paint. It was not found necessary to paint the inside of the reaction chamber black.

The plate at the base of the lens assembly contained a rectangular hole cut through its centre to allow fluorescence to pass through the lens assembly towards the detector. Several plates were made with different hole sizes. Originally a hole size of 20 mm $\times$ 10 mm was used, this was changed to 10 mm $\times$ 5 mm to reduce the level of scattered light seen by the detector. This measure did not reduce the LIF signal.

The greatest reduction in scattered laser light was achieved by placing an appropriate bandpass interference filter between the focussing lens and the PMT. The interference filter was chosen to transmit radiation over the wavelength region of the desired vibronic transition, whilst blocking both the photolysis and probe laser wavelengths. Two bandpass interference filters were used in this work; an Ealing 35-8044 centered at 310 nm with a bandwidth of 10 nm and a Melles Griot O3FIM018 centered at 280 nm with a bandwidth of 10 nm.

2.3.1 Photomultiplier Tube

A single PMT was used for all the LIF experiments (Thorn EMI 9789QB). The tube was chosen because of its relatively high response in the wavelength region

of interest: over the range 275-340 nm the quantum efficiency rose monotonically from ca. 20% to 25%. The 9789QB had a nominal 10 ns response time and a 20 ns FWHM pulse width at normal operating temperatures. The tube had a venetian blind dynode system (13 stages) and an effective 10 mm CsSb photocathode diameter. The relatively small photocathode diameter produced low dark currents at low light levels. Signals from the PMT were amplified and detected by the same combination of electronics as ion signals from the MCP.

2.4 Gas Handling

The vacuum apparatus was connected to a gas inlet system. This allowed the gases of interest to be introduced into the reaction chamber.

There were two separate lines leading to the reaction chamber (one for the photolysis precursor reagent and one for the molecular target reagent). The gases were stored in stainless steel reservoirs (Whitey, 1 litre) and could be purified by freeze-pump-thaw cycles.

Gases could be introduced into the reaction chamber either via effusive sources or pulsed molecular beam valves.

2.4.1 Effusive Sources

The simplest of these involved bleeding gases in via the rear flange of the reaction chamber as shown in the upper panel of figure 2-4. This was sufficient when the transition being studied was fairly intense and the number density of the species was high. However, for weaker signals a more direct source was used as shown in figure 2-5. In this case glass injectors drawn to various hole sizes were used to feed the reagent(s) into the reaction chamber at a point approximately 2 mm from the laser beam(s). This increased the local density at the observation point by a factor of approximately 30 for a given total background pressure in the reaction chamber.

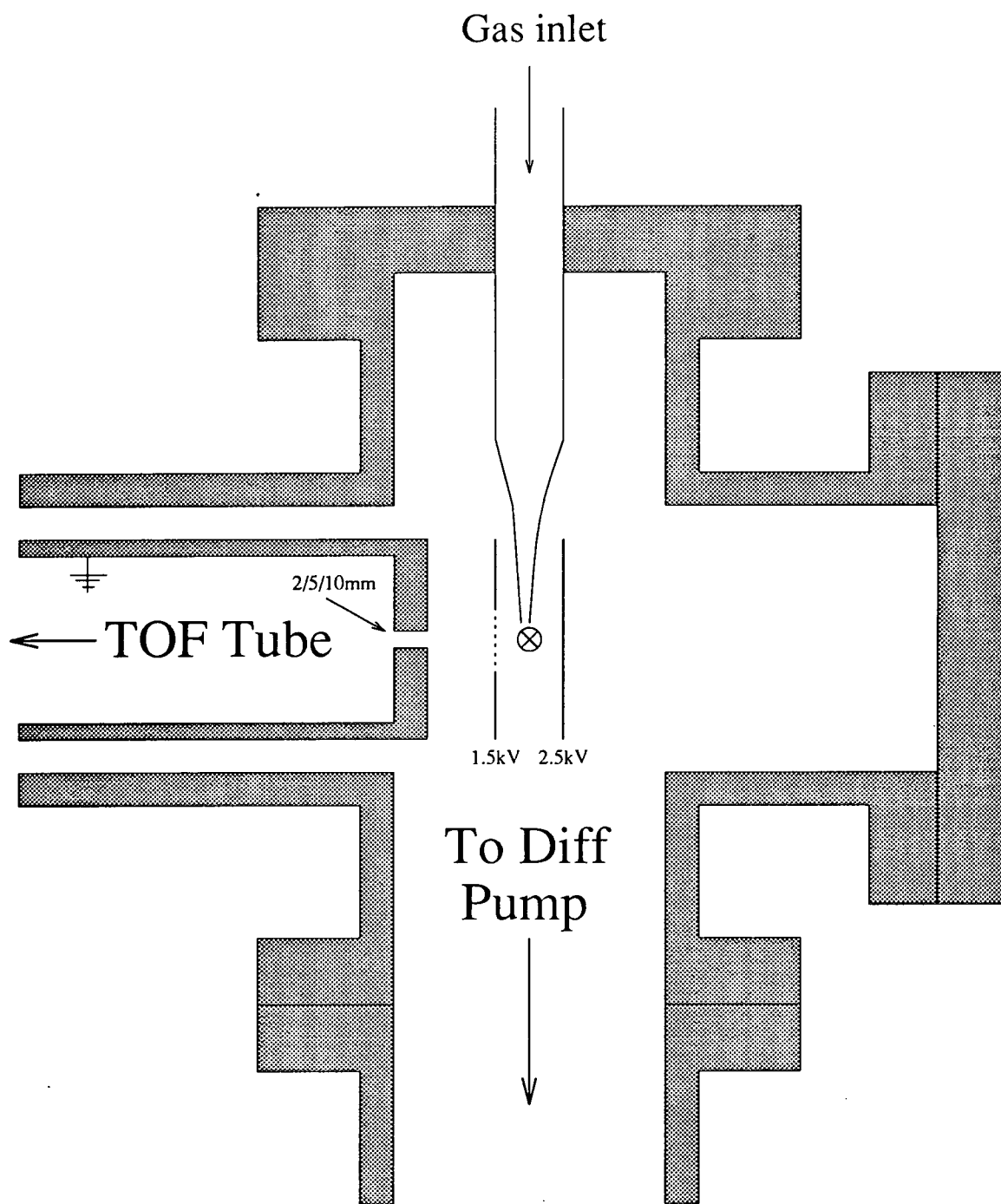


Figure 2–5: Schematic of the reaction chamber with gas entering via a gold coated glass capillary tube.

In REMPI experiments the bottom 5 cm of the glass injectors were coated with gold and could therefore be electrically floated. They were floated at a carefully tuned voltage which was approximately half the potential between the repeller and retarder plates. This proved to be successful in avoiding any problems with ion extraction caused by field distortion. A separate high voltage power supply was used for this purpose (Stanford Research Systems, model PS350, 0-5 kV)

2.4.2 Pulsed Molecular Beam Valve Source

The gas number density at the interaction zone between the laser(s) and gas(es) could be increased further by using a pulsed molecular beam valve.

The pulsed molecular beam valve used in this work was a General Valve Corporation Series 9 valve. The valve consisted of an iron actuator, with a Teflon plunger attached, which sealed against the orifice of a flange screwed on to the bottom of the valve. Three flanges were available, with orifice diameters of 0.15, 0.5 and 0.8 mm. The valve was opened by application of a current pulse to a single solenoid, which had the effect of pulling back the actuator. The resultant gas pulse duration was determined by the length of time the current was applied to the actuator. The current pulse was supplied by an Iota One valve driver (also supplied by General Valve Corporation).

Figure 2-6 shows a diagram of how the valve was arranged within the reaction chamber. The valve was mounted on a custom built flange supplied by Vacuum Generators, UK, Ltd. The valve was connected to the centre gas inlet port via stainless steel tubing. The valve could be adjusted vertically, allowing the valve to laser distance to be varied.

The single valve configuration was intended to be used for bimolecular experiments where the precursor and reactant gases were unreactive with each other and could be pre-mixed.

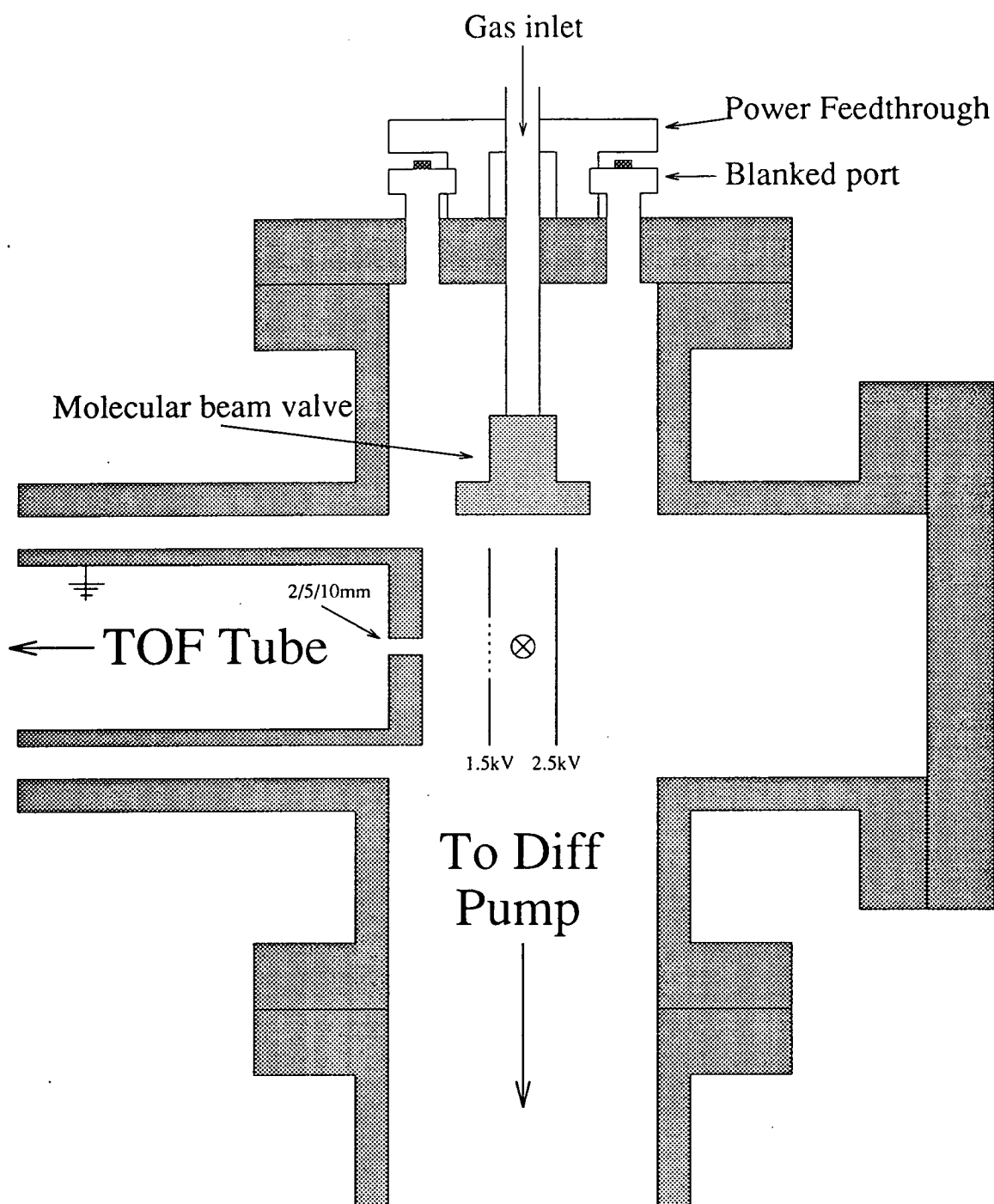


Figure 2-6: Schematic of the reaction chamber with gas entering via a single molecular beam valve.

2.5 Radical or Atomic Sources

An essential requirement for experiments carried out in this thesis was the production of radicals or atoms. Two methods were used for the production of such species;

1. microwave discharge of a suitable precursor molecule
2. laser photolysis of a suitable precursor molecule

2.5.1 Microwave Discharge

The use of microwaves as sources of a discharge can present significant advantages over other conventional sources.

- the cavity is electrodeless and is free from the problem of introducing additional impurities. Normally the cavity will also have a much longer lifetime than one which contains electrodes.
- A microwave cavity is relatively safe since it produces only weak fields.
- The discharge is typically efficient, producing a high degree of dissociation even at low powers.
- The microwave generator produces very little electrical interference, unlike for example a radio frequency discharge.

The degree of dissociation induced in the reagent gas by a discharge has been extensively studied[4]. There is general agreement that the degree of dissociation will depend on the following factors;

- the total pressure and flow rate of the gas
- the purity of the gas
- the temperature and chemical nature of the walls of the discharge tube

- the power being coupled into the discharge

Figure 2-7 shows the experimental set up used in this work for carrying out microwave discharge experiments. An EMS Microtron Mk 3 microwave power supply producing microwaves at 2450 MHz[3] was used. The discharge cavity, EMS 214L, was operated at powers between 15 and 75 Watts depending on the molecular precursor. The cavity was air cooled. The reflected power from the cavity was measured using an EMS reflected power meter.

The inner discharge injector was made of quartz and was internally coated with ortho-phosphoric acid to cut down heterogeneous loss of radicals. Molecular reagents flowed through the outer injector and were allowed to mix and react with the radical species formed in the discharge. The outer injector was made of glass and was internally coated with halocarbon wax. The bottom 5 cm of the outside of the outer injector was gold coated and electrically floated to allow close access to the laser focus while minimising field distortion. The outer injector could be moved vertically relative to the laser beam and the internal injector could be moved vertically relative to the outer injector.

2.5.2 Laser Photolysis

In this work laser photolysis of a suitable precursor molecule was the most desirable method of producing atoms or radicals.

The main desirable features of pulsed laser photolysis are:

- the high density of species which may be produced effectively instantaneously
- the non-thermal atomic translational energy distributions produced result in non-thermal collisions between the hot atoms and target reactant molecules
- polarised laser photolysis creates an anisotropic distribution of fragment recoil velocities and hence of collision velocities
- fast, high resolution detection methods provide an opportunity to study final quantum states on a timescale fast enough to determine nascent populations

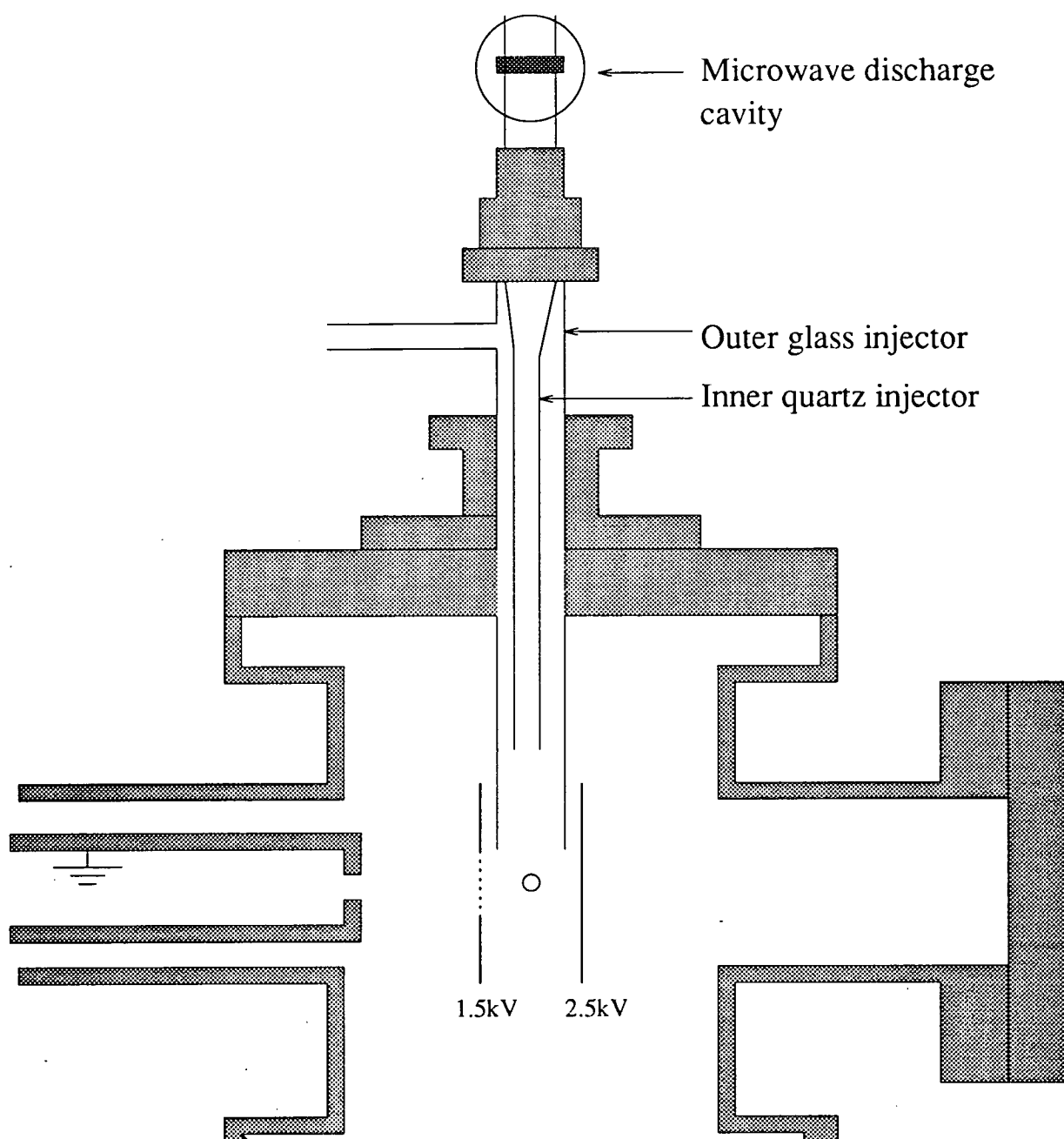


Figure 2-7: Schematic of the reaction chamber and the microwave discharge apparatus used for generation of radicals and atomic species.

of individual vibrational and rotational levels for product species resulting from a single hot atom/reactant encounter.

The degree of dissociation depends on the molecular extinction coefficient, at a particular photolysing wavelength, and on the photon intensity of the photolysis laser beam.

Figures 2-8 and 2-9 show the apparatus used to do a photolysis/probe experiment incorporating either REMPI or LIF detection. The species to be photolysed is introduced into the reaction chamber via either effusive or pulsed sources. The probe laser entrance window was set at Brewster's angle to ensure the maximum transmission of the polarised probe light. The photolysis and probe beams counter-propagated each other. Whether or not either of the beams was focused depended on the molecule being studied. Quartz lenses were used to focus the photolysis or probe beams and were usually mounted externally to the vacuum system, but could be mounted internally via mounts attached to the inside of the entrance and exit flanges of the reaction chamber.

2.6 Experimental Control and Data Acquisition

A hot atom dynamics experiment requires precise control of the sequence of several experimental events, and generates a large amount of data which must be processed in a short period of time. It therefore requires a sophisticated computer-based system to facilitate optimisation of the experimental parameters and to acquire and store data.

Before describing the instrumentation and computer hardware to control the experiment, it is useful to outline the experimental cycle used in this work.

2.6.1 Experimental Cycle

The entire experiment was driven by software written by a colleague[5], implemented on an IBM PC-AT. This software controlled experimental timings and acquired data, via a CAMAC interface.

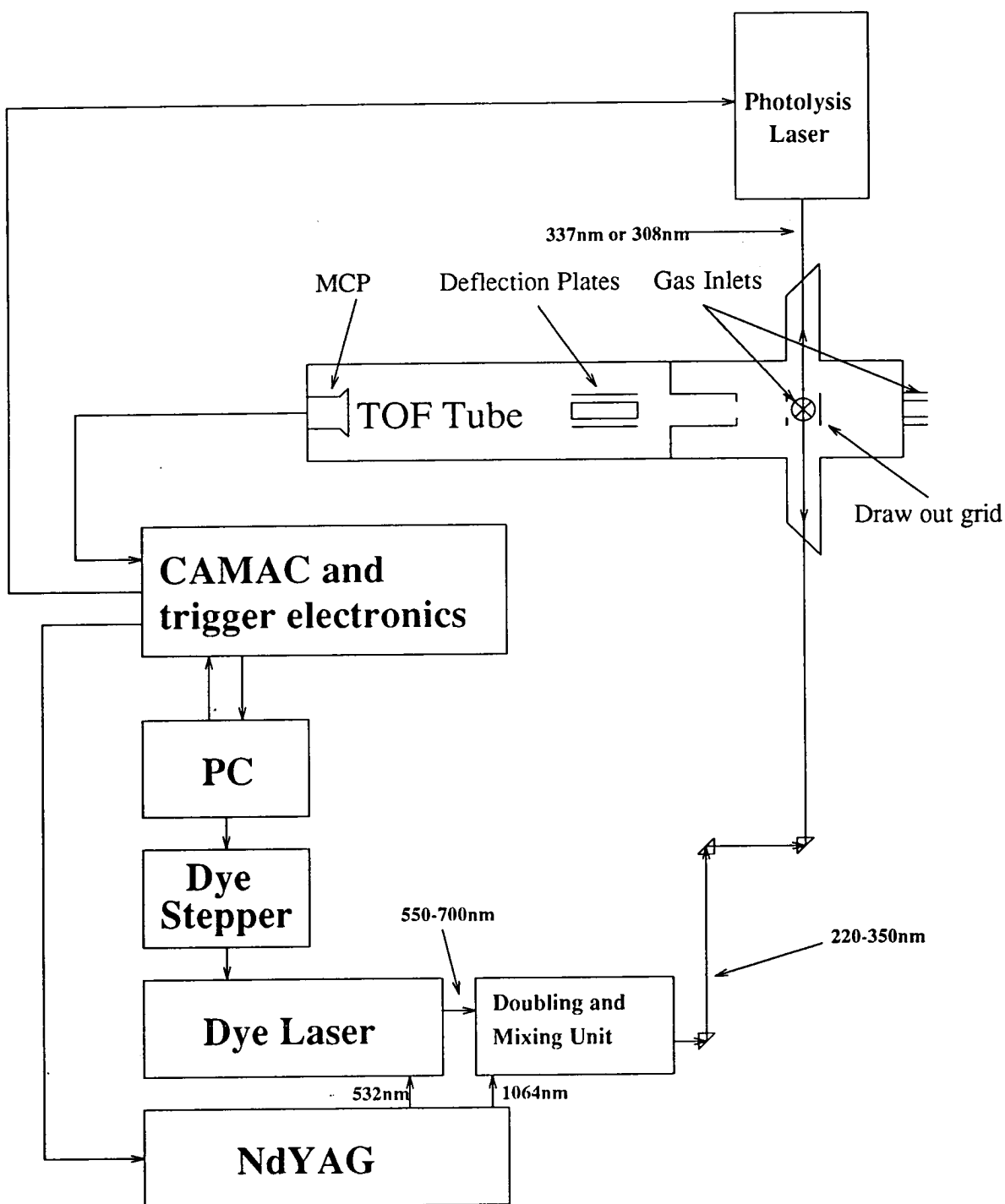


Figure 2-8: Schematic of photolysis/probe apparatus incorporating REMPI detection

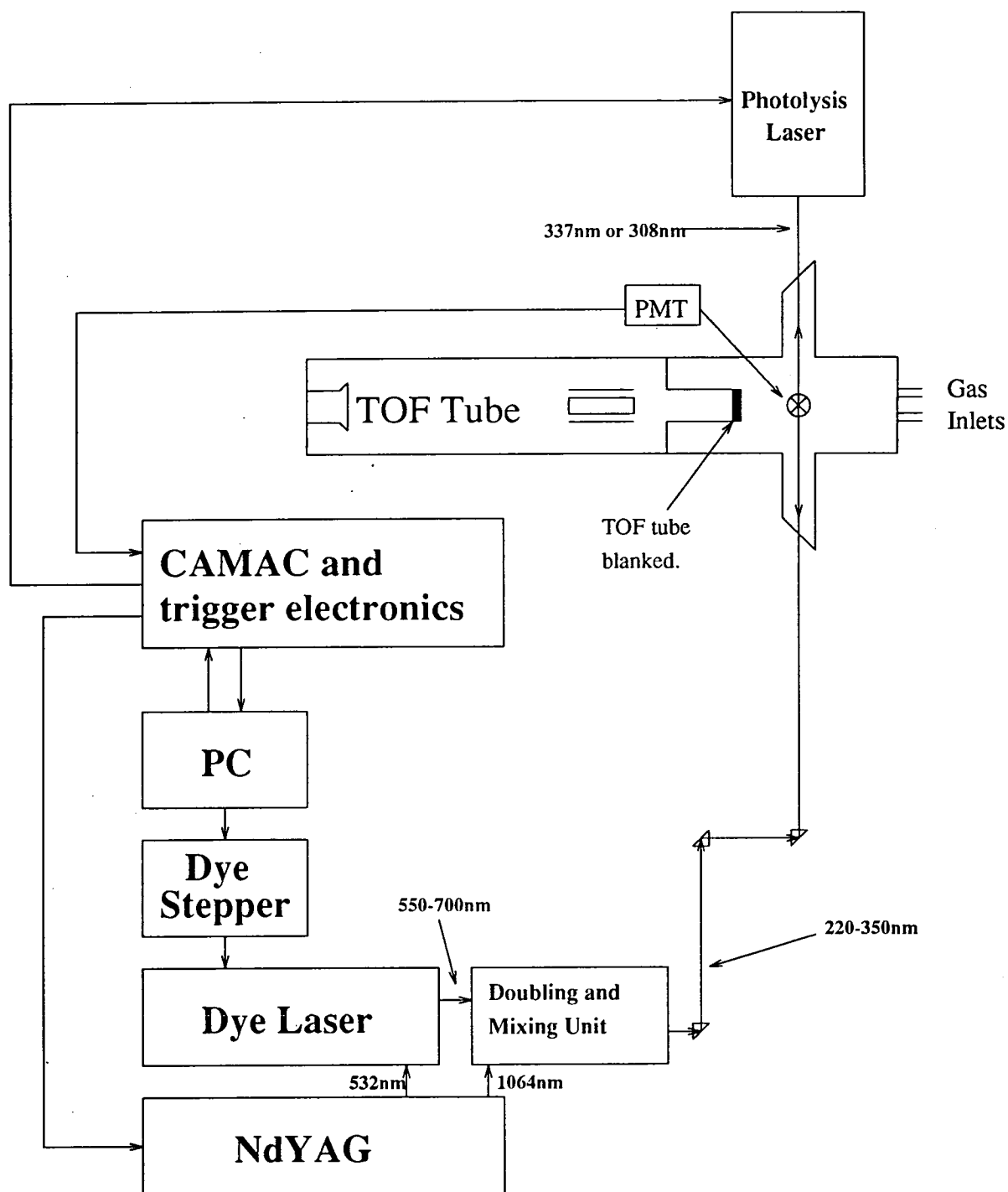


Figure 2-9: Schematic of photolysis/probe apparatus incorporating LIF detection

A constant repetition rate was accomplished by employing the interrupt mechanism of the PC-AT. The interrupt was generated at 20Hz, twice the desired experimental rate. On alternate interrupts, the software toggled between controlling the experimental apparatus and processing the data.

When controlling the experimental apparatus the PC-AT sent signals through a CAMAC dataway to trigger a pulse generator. The pulse generator delivered trigger pulses to various items of the experimental apparatus in an appropriate sequence. The most sophisticated timing sequence used in this work was for a two laser experiment employing a pulsed molecular beam valve. A timing set up is given in figure 2-10 for such an experiment. The schematic illustrates the need for 3 separate, variable time delays. These were:

1. Δt_1 , the time delay between the molecular beam valve opening and the Q-switch firing (i.e. the probe laser).
2. Δt_2 , the time delay between the gas-discharge laser firing and the Q-switch firing (to control the photolysis-probe time delay).
3. Δt_3 , the time delay between the start and stop pulses of the transient digitiser (to make sure data captured is that containing probe-induced signal).

The flashlamps and Q-switch were fired at fixed times because this delay has to be at the optimum for maximum gain. The double headed arrows shown on figure 2-10 represent channels whose time delays could be varied.

In summary, the experimental cycle was initiated by the firing of the pulsed valve. After a suitable delay the gas-discharge photolysis laser was fired. After a second experimentally controlled delay the probe laser was fired. The time delay between the photolysis and probe lasers firing was verified using a fast response photodiode. The signal generated by the experiment was detected and amplified then fed into the input of the TD. A stop pulse was then sent to the TD which prompted the TD to digitise the ion or fluorescence signal. In between experimental cycles the digitised data, stored by the TD, was downloaded into a temporary buffer file in the PC-AT for processing.

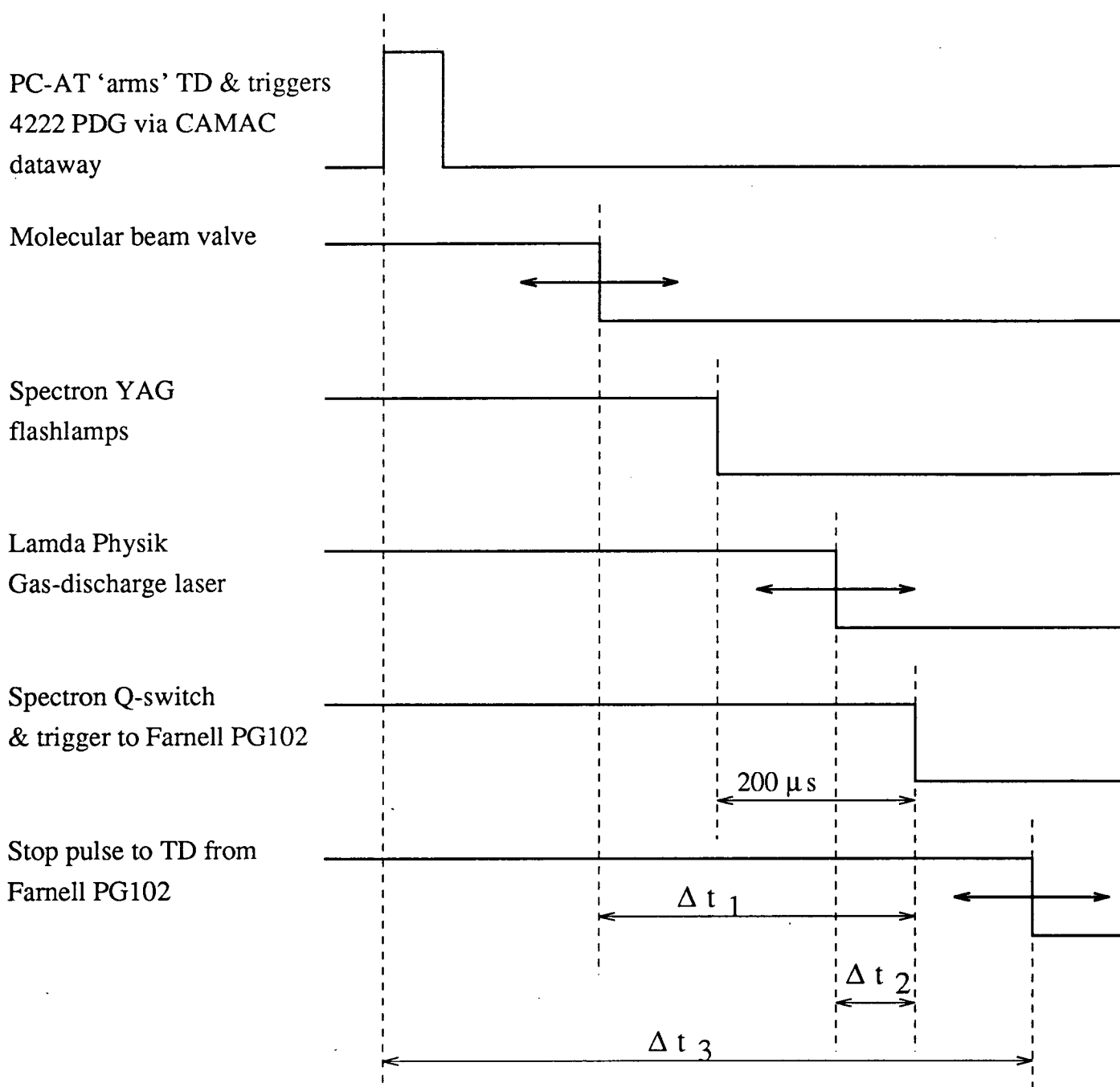


Figure 2–10: Schematic of the timing sequence for a 2 laser, molecular beam valve experiment

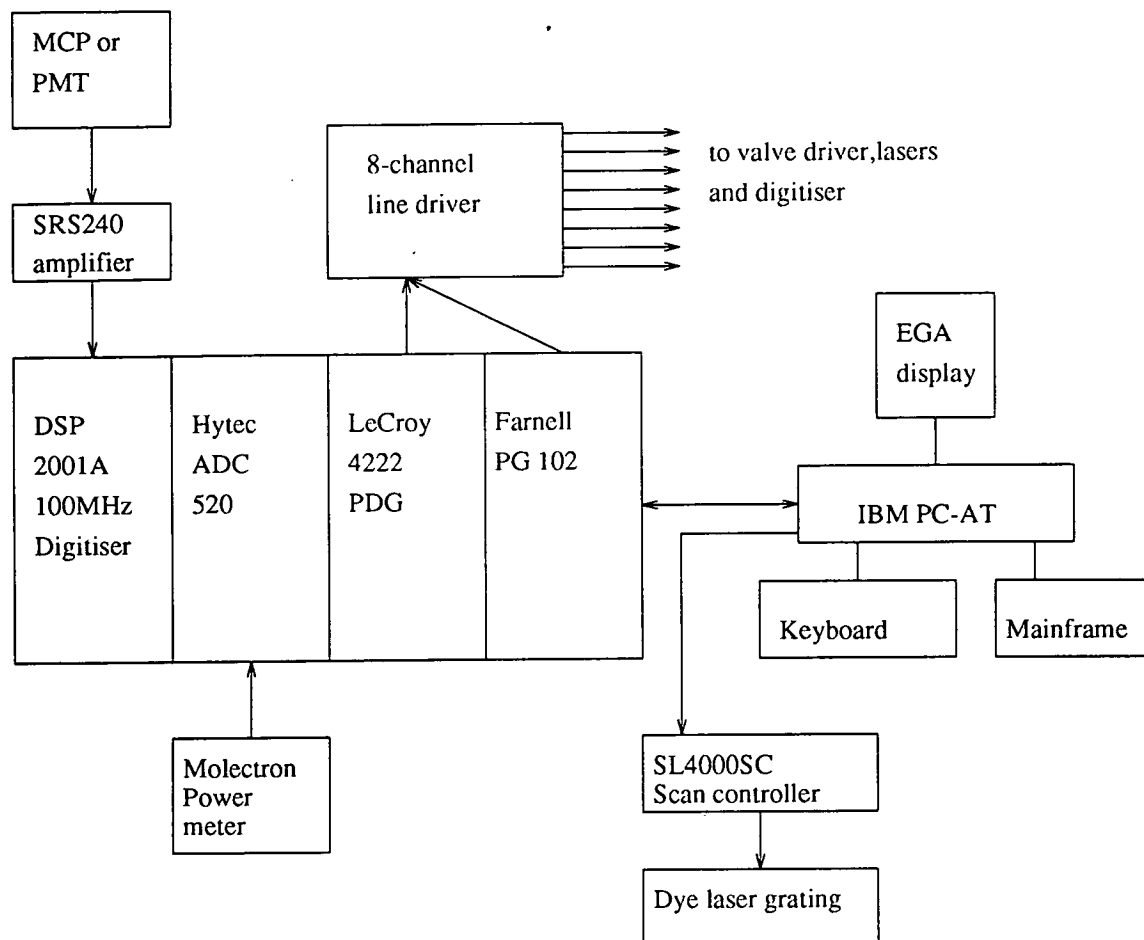


Figure 2-11: Schematic of the CAMAC based experimental control system

2.6.2 CAMAC Crate

The IEEE CAMAC standard[6] defines a common dataway to which a number of instruments can be interfaced. All the CAMAC instruments were located in a crate (Optima 860), whose backplane provided data communication and power lines to each module. A common dataway of 24 read/write lines was used to transmit data to and from the units. Other data lines directed commands from the software implemented on the IBM PC-AT to the correct module or part of a module and transmitted acknowledgements of receipt of these commands or requests for attention by each module to the microcomputer.

As shown in figure 2-11 the crate contained several instruments for controlling the experimental timings and acquiring data. These will be discussed individually below.

2.6.3 IBM PC-AT Microcomputer

The IBM PC-AT contained an Intel 80286 (16 bit) processor, clocked at 8 MHz, an 80287 maths co-processor and 640kb of RAM. Experimental data was displayed on a high resolution VDU, driven by an EGA 256 kb graphics card. A 20 Mb hard disk and a 1.2 Mb floppy drive allowed storage of software and data.

2.6.4 DSP 6001 Crate Controller

This dedicated microprocessor, which was programmed through a DSP PC004 interface card located in an 8 bit expansion card slot in the PC-AT, accepted commands from the computer then passed these on to the appropriate modules within the crate. It also passed data recorded by the modules back down the dataway to the PC-AT for further processing.

2.6.5 Pulse Delay Generators

Two pulse delay generators provided the necessary trigger pulses required to run experiments. These were a LeCroy 4222PDG and a Farnell PG102.

The LeCroy PDG had four channels which could each produce four 100ns FWHM TTL pulses of 1ns accuracy. It was triggered by an instruction passed through the dataway from the PC-AT. The 4222 was used to trigger devices where very precise control of timing was required.

The Farnell PG102, which is not part of the CAMAC control system, is a stand alone pulse generator which had two channels which could produce 0.1 microsecond FWHM TTL pulses. Consequently it was used for triggering devices which required less stringent timing accuracy.

Futhermore, some of the devices required trigger levels higher or longer than those generated by the pulse generators. The outputs of the pulse generators were boosted by a custom built 8 channel line driver unit, housed in a NIM bin, which could produce either a 5 V, 10 μ s pulse or a 15 V, 50 μ s pulse or a 20 V, 50 μ s pulse.

2.6.6 DSP 2001A Transient Digitiser

The arrival of ions at the microchannel plates or photons at the photomultiplier tube, generated a waveform consisting of a series of negative-going peaks. Digitisation of this signal required the use of a fast sampling device, namely the DSP 20001A TD. This device had 8 bit resolution with a maximum input voltage of 512 mV, giving a minimum detectable change of 2 mV. The digitising rate could be set between 1 and 100 MHz. The memory of the TD was divided into different record lengths, selectable in powers of two from 256 bytes to 32 kb. The maximum record length that could be easily processed at the interrupt frequency of 20 Hz was limited to 4096 samples. This was perfectly adequate for the experiments carried out.

The TD was armed by a CAMAC dataway command. The input signal was continuously sampled and stored in the chosen fraction of available memory. This data was constantly overwritten, until the receipt of an external stop trigger pulse. The next batch of samples then constituted the required mass spectrum or LIF fluorescence decay signal.

2.6.7 Hytec ADC 520 Analogue to Digital Convertor

While the TD performed the necessary fast waveform sampling function, there were other sources to be monitored during an experiment, particularly for power normalisation purposes. The ADC 520 consisted of four channels each with a conversion time of approximately 20 microseconds.

2.6.8 Control Software

The use of a CAMAC based system, in which much of the control and signal processing is carried out external to the computer, greatly reduces the requirements placed on the software itself.

The control software had to perform several functions. Firstly, it had to provide some means of setting the parameters for and monitoring the output from the various devices under its control, particularly the CAMAC modules and the laser

system. Secondly, it had to synchronise all active modules while the dye laser was scanning.

For the present work the main source of data was the transient digitiser. Having recorded the required number of waveform samples the data was then down-loaded to the PC for processing. The processing stage consisted of integrating discrete segments of the waveform (with background subtraction) and saving the processed data.

The code for setting up the digitiser allowed the waveform output of the digitiser to be monitored in real time for short record lengths. Gates could then be set specifying start and stop points for integration (i.e. for different mass channels in REMPI or over a certain time range of a fluorescence decay signal). Background subtraction gates, one for each signal gate, also had to be specified.

For very light ions in REMPI experiments or for fluorescence decay profiles in LIF experiments, the signal was often difficult to observe due to an overlap of the signal with the Q-switch noise from the Nd:YAG laser. To monitor the signal only a number of waveforms with no signal other than the background were multiplexed, the resulting waveform was then subtracted from the signal bearing waveform on a shot-to-shot basis.

The control software was designed to record spectra for different time delay settings simultaneously. A maximum of ten delay sets could be active at any one time with the trigger code automatically cycling through the delay sets on successive laser shots. Using the delay sets in this manner ensured that spectra collected were all directly comparable since no single spectrum would suffer excessively from long term changes in the experimental conditions.

The software also allowed different wavelength ranges to be recorded under the same experimental conditions. This was advantageous where lines far apart in wavelength were being compared.



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Chapter 3

Spectroscopy of the OH Radical

3.1 Introduction

The OH radical is one of the most exhaustively studied reactive species in the gas phase, being of prime importance in combustion systems and atmospheric chemistry. Experiments on these systems usually rely on detection of OH by LIF on the well known, one photon $A^2\Sigma^+ \leftarrow X^2\Pi$ transition near 305nm. Whilst LIF provides a very sensitive means of detecting OH, the low transition moment and relatively long lifetime ($= 0.7\mu\text{s}$) combined with efficient electronic quenching reduce the sensitivity, particularly at higher pressures. Moreover the Franck-Condon matrix for this transition is nearly diagonal, making it difficult to discriminate against the excitation wavelength and reducing the absolute detection limit. In the case of reaction dynamics experiments, where OH may be created in a high angular momentum state, the predissociation of the $A^2\Sigma^+$ state above $J'' = 23$ in $v'' = 0$ and above $J'' = 14$ in $v'' = 1$ limits the quantum states that may be observed.

REMPI can provide an alternative detection technique which may be more convenient in certain circumstances. At low number densities the ability to detect single ions free from interference from scattered laser light offers REMPI detection a greater sensitivity than LIF.

The purpose of this chapter was to compare the relative advantages and disadvantages of detecting the OH radical by either REMPI or LIF to decide which method would be best employed for a hot atom dynamics experiment producing OH as a nascent reaction product.

3.2 The (2+1) REMPI Spectroscopy of the OH Radical

3.2.1 General Spectroscopic Considerations

The states of interest are described via differing approximations of the way angular momenta couple in a molecule (Hund's cases). The various angular momenta are defined as follows:

- S is the electronic spin angular momentum
- L is the electronic orbital angular momentum
- J is the total angular momentum
- N is the total angular momentum excluding electronic spin ($N=J-S$)
- R is the nuclear rotational angular momentum ($R=N-L$)

In a Hund's case (a) basis, L and S are coupled to the internuclear axis and thus have projection quantum numbers on this axis of Λ and Σ respectively. The resultant $|\Lambda + \Sigma|$ forms the projection quantum number Ω . The total angular momentum J is therefore the sum of $|R + \Omega|$ and this makes the projection M on the space fixed Z axis.

Hund's case (b) differs primarily from case (a) in that the spin vector S is not coupled to the internuclear axis. In this case the projection quantum number Λ and R couple to form a resultant N. N then couples with S to form the total angular momentum J, which again has the projection M on the space fixed Z axis. When the spin-orbit interaction is strong Λ and Σ are not defined and only the total electronic angular momentum Ω is defined. The nuclear rotation R then adds vectorially to Ω to make the total angular momentum J.

Up to the present, only six electronic states of OH are known[1]. The ground configuration of OH is $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^3$ which produces the $X^2\Pi$ ground

electronic state. Spin-orbit coupling in the $X^2\Pi_i$ state of the OH radical causes it to be split into two components. The $\Omega = 3/2$ component is the lowest member of the doublet, the $\Omega = 1/2$ component lies 123 cm^{-1} higher[2]. The low rotational levels of the this state conform to a coupling scheme intermediate between Hund's case (a) and (b). For higher rotations the spin is uncoupled from the internuclear axis and the coupling scheme approaches Hund's case (b).

The A , B , and C states are $^2\Sigma^+$ valence states. Until recently the only observed transition to a Rydberg state was the single photon VUV $D^2\Sigma^-(v'=0) \leftarrow X^2\Pi(v'' = 0)$ transition (the $D^2\Sigma^-(v'=0)$ state has electronic configuration $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^2(3p\sigma)^1$ with a ground state $X^3\Sigma^-$ ion core). However, two papers published only weeks apart[1][3], reported the identification of the higher $D^2\Sigma^-(v'=1,2)$ levels and the previously unobserved $3^2\Sigma^-(v'=0)$ state. These new transitions were observed via the (2+1) REMPI of OH.

Reference to figure 3-1, which shows the lower lying $^2\Sigma^-$ and $^2\Sigma^+$ states of OH, illustrates why these previously unobserved states become accessible via the (2+1) REMPI of OH. The A state is not suitable for REMPI since it is a valence state and requires three more photons for ionisation. The B and C states both have large equilibrium bond lengths ($r_e=1.87$ and $2.05\text{\AA}$ respectively, compared to the ground state value of $0.97\text{\AA}$) and cannot be accessed from the lower vibrational levels of the ground state. By contrast, values of $r_e=1.08$ and $1.25\text{\AA}$ for the $D^2\Sigma^-$ and $3^2\Sigma^-$ states make transitions from the $X^2\Pi(v'' = 0)$ level accessible.

3.2.2 Production of OH Radicals

Hodgson *et al*[3] generated the OH radical via the one photon laser photolysis of hydrogen peroxide. The same laser beam then probed the OH fragment via (2+1) REMPI. Since the absorption coefficient for hydrogen peroxide is almost constant over the wavelength region studied[4], the intensities in their REMPI spectra were not strongly influenced by the variation of OH production. De Lange *et al*[1] generated the OH radical by photolysis of hydrogen peroxide and formic acid. In both cases the same laser used to photolyse was also used to probe.

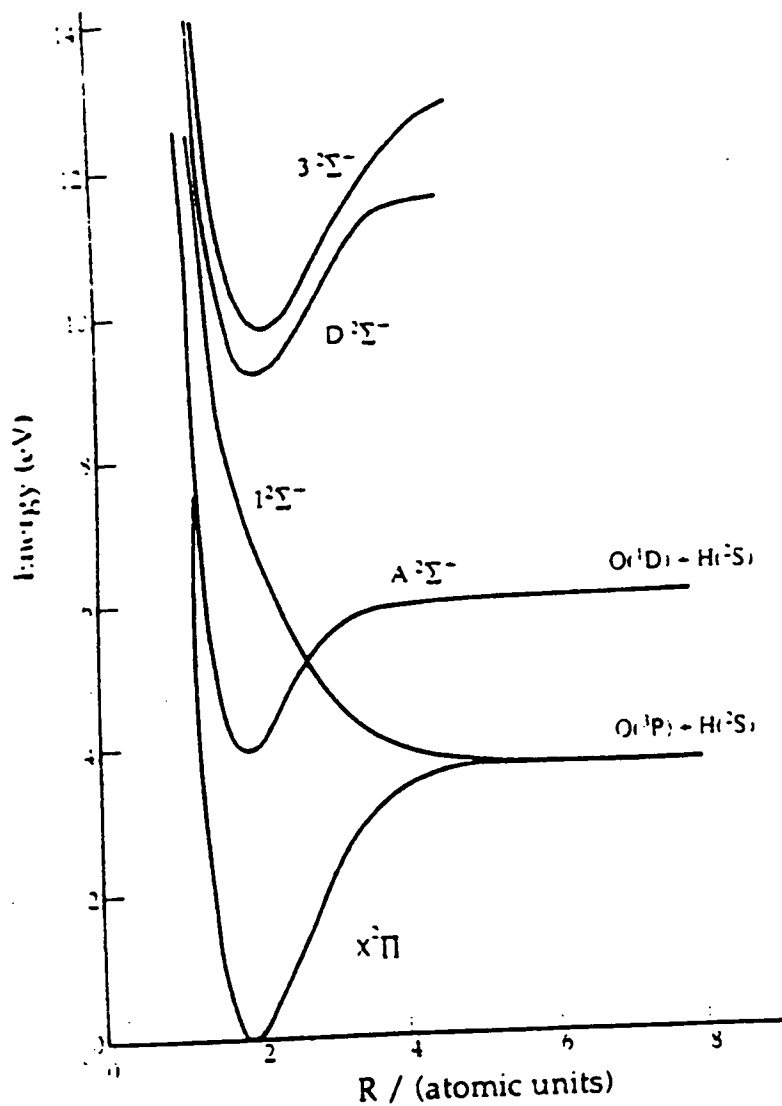
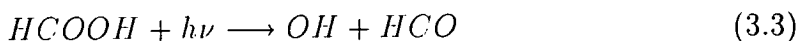
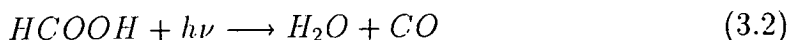


Figure 3-1: Selected potential energy curves for OH from reference [3]

For formic acid there are three possible dissociation channels after photoabsorption.



Equation (3.3) has been found to be the main process[5]. Formic acid is known to dissociate via the S_1 excited state in the 200-260 nm wavelength region, which exhibits well developed vibrational structure superimposed on a diffuse background which merges to a continuum at a wavelength of ≤ 200 nm[6]. The intensities in the associated REMPI spectra may therefore be influenced somewhat by the wavelength dependence of the absorption cross section.

The rotational linestrength factors and selection rules for a 2-photon absorption process have been presented before[7]. These derivations were based upon the assumption that the transition involved two states of Hund's case (a) coupling. The 2-photon absorption process for OH is complicated further by the fact that the ground electronic state is a doublet state with rotational levels conforming to a coupling scheme intermediate between Hund's case (a) and (b). Zacharias[8] has derived the rotational line intensities and selection rules for 2- and 3-photon excitation of doublet states belonging to Hund's case (a) or (b), or to the intermediate (a)-(b) case. These results have been generalised further by Manios[9] for an n -photon absorption process.

The rotational selection rules for two photon transitions are $\Delta J = 0, \pm 1, \pm 2$. For pure Hund's case (b) the selection rules are $\Delta N = 0, \pm 1, \pm 2$. In Hund's case (a) the quantum number N is not defined and hence the selection rules for ΔN do not hold. Transitions satisfying both ΔJ and ΔN selection rules between $^2\Pi$ and $^2\Sigma^-$ states give rise to 12 strong branches. Transitions not obeying the ΔN selection rules only have appreciable probability as long as N is not a good quantum number. Therefore the 8 branches violating the ΔN selection rules are very weak except for small values of N where the coupling is still intermediate between Hund's case (a) and (b).

3.3 Experimental Procedure

We planned to detect the OH radical using (2+1) REMPI via the $D^2\Sigma^-(v'=0) \leftarrow X^2\Pi(v''=0)$ and $3^2\Sigma^-(v'=0) \leftarrow X^2\Pi(v''=0)$ transitions employed by Hodgson[3] and de Lange[1]. This meant generating one photon laser wavelengths in the regions 243-246 nm and 227-230 nm, which was achieved by doubling the output of the dye laser (DCM dye for $D^2\Sigma^-(v'=0) \leftarrow X^2\Pi(v''=0)$ transition and a rhodamine 590/610 dye mixture for the $3^2\Sigma^-(v'=0) \leftarrow X^2\Pi(v''=0)$ transition) then mixing the doubled output with the 1064 nm fundamental wavelength of the Nd:YAG laser. The final doubled/mixed beam had an energy of ~ 1 mJ per pulse and was focused by an appropriate lens into the reaction chamber through Brewster angled entrance and exit windows.

We chose to generate the OH radical via two methods

1. the one photon photolysis of formic acid
2. the $\text{H} + \text{NO}_2 \longrightarrow \text{OH} + \text{NO}$ chemical reaction

The first option was chosen to test whether we could replicate the results of Hodgson and deLange, whereas the second option was chosen to see whether a more productive source of OH could be established.

3.3.1 Photolysis of formic acid

Although photolysis of hydrogen peroxide would seem a better choice to generate OH (because it has an almost constant absorption coefficient over the wavelength region of the two REMPI transitions) we chose formic acid because it is much easier to handle (hydrogen peroxide is readily decomposed by metals and would therefore be difficult to handle within our stainless steel vacuum system).

Formic acid is a liquid at room temperature and atmospheric pressure, with a boiling point of 100.7°C [10]. The formic acid (Fisons, 98% purity) was admitted into the vacuum chamber via a needle valve, through the back flange of the reaction

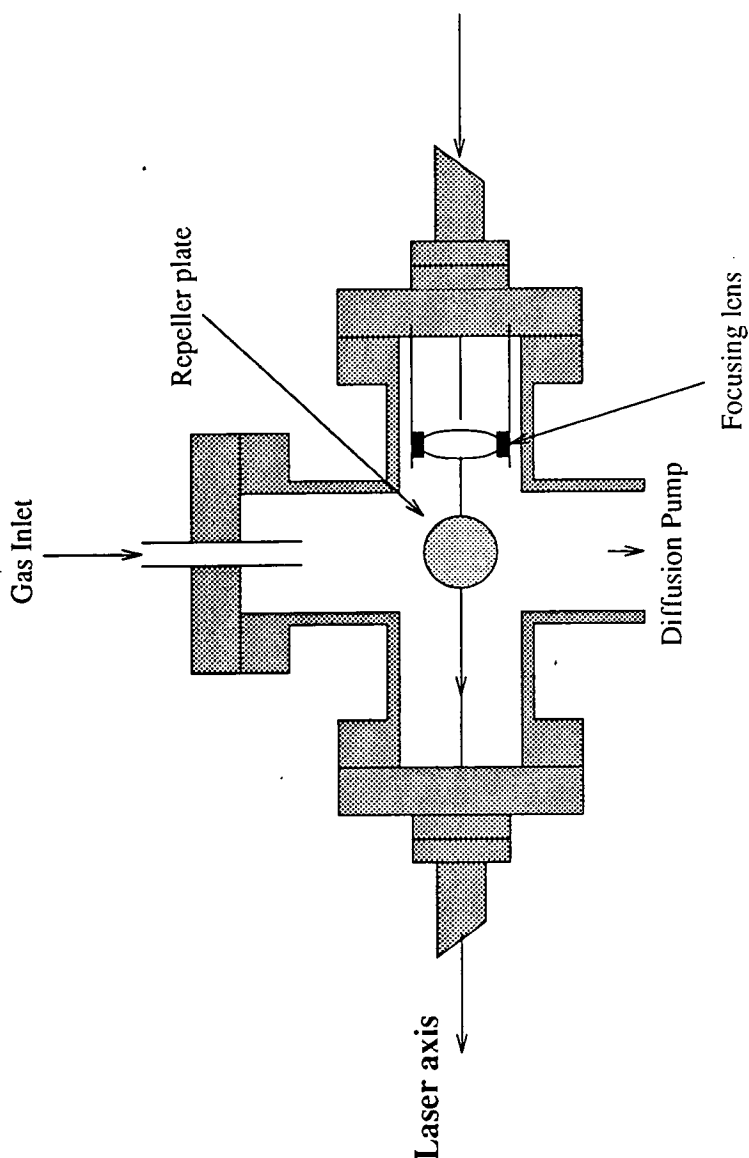


Figure 3-2: Schematic of the apparatus used for the (2+1) REMPI of OH showing the positioning of the focusing lens within the reaction chamber.

chamber. Typical pressures in the reaction and detection chambers were 1 mTorr and 1×10^{-6} mbar respectively.

The photolysis/probe of formic acid involved the absorption of four photons from a single laser beam (one for photolysis, two for resonant absorption and one for ionisation) therefore it was necessary to use a shorter focusing lens to increase the photon intensity at the laser-gas interaction region. A 6 cm quartz lens was used. Due to the geometry of the vacuum apparatus the lens had to be positioned within the reaction chamber, this is shown schematically in figure 3-2.

3.3.2 $\text{H} + \text{NO}_2 \longrightarrow \text{OH} + \text{NO}$

This experiment was carried out using the microwave discharge apparatus described in section 2.5.1. The reader is referred back to figure 2-7, which shows a schematic of the apparatus used.

What follows is a brief summary of the procedure used for this experiment. (A fuller description of a similar type of experiment is given in chapter 6).

The $\text{H} + \text{NO}_2 \longrightarrow \text{OH} + \text{NO}$ reaction is widely used as a source of OH for gas kinetic studies[11][12]. We hoped that it might provide a better source of OH radicals than formic acid photolysis and since the OH REMPI signal should have a decreased laser power dependence (no photolysis step required) we might also expect an increase in the signal to noise ratio for OH detection. Hydrogen atoms were produced by the microwave discharge of molecular hydrogen in argon (1:1 ratio of H_2 :Ar). A microwave power of 50 W was used for a pressure of 1-2 Torr in the quartz discharge inner injector. NO_2 (Matheson, 98.5% purity) was admitted through the sidearm of the outer injector and was allowed to pre-mix with the hydrogen atoms generated by the microwave discharge. 1:1 flows of H_2 Ar: NO_2 were used resulting in a total pressure of 5×10^{-5} mbar within the reaction chamber.

The laser was aligned relative to the top hat hole (which separates the reaction and detection chambers) to ensure that the maximum number of ions were transmitted to the detector. The outer glass injector could be moved relative to the focus of the laser beam. Placing such an insulator in the electrical fields of the extraction region required the outer injector to be electrically floated to maintain the uniformity of the extraction fields. The inner injector could be moved within the outer injector.

For both methods of generating OH, the resonant, mass resolved $m/e = 17$ ion signal was collected.

3.4 Results and Discussion

3.4.1 Photolysis of formic acid

Figure 3-3 shows the time-of-flight spectrum obtained via the photolysis of formic acid. This spectrum shows the parent molecular ion, HCOOH^+ , as well as all of the expected fragments; OH^+ , HCO^+ , CO^+ , H_2O^+ , CO_2^+ . It was recorded at a laser wavelength of 244.238 nm, which corresponds to the $R_1(1)$ line of the $D^2\Sigma^-(v'=0) \leftarrow X^2\Pi(v''=0)$ band of OH.

The relative sizes of the fragment ion signals shown in figure 3-3, agree with reference [5] i.e. the main product channel in the photolysis of formic acid produces OH and HCO. The presence of the bare carbon ion signal has resulted from further fragmentation of the main photolysis products, which was to be expected at the high laser intensities used.

The OH mass channel was the only resonant signal. From figure 3-3 it can be seen that the non-resonant HCO signal is approximately the same size as the OH signal. This does not present serious problems in this particular experiment, however in dynamics experiments producing low concentrations of nascent products, it may seriously limit our ability to monitor weak signals in the presence of much larger background signals. This led us to develop a pulsed deflection field into the flight tube of the apparatus to prevent large, unwanted ion signals, such as non- or near-resonantly ionised species with relatively low ionisation potentials reaching and overloading the microchannel plate detector.

The design of the “pulser” or “ion shutter” was based on an original design by Zare[13]. We used the existing deflection plates (section 2.2.3) along with a home built electronic device which allowed the voltage applied to the deflection plates to be pulsed rather than continuous.

The “ion shutter” constructed took a d.c. voltage input from a $0 \rightarrow \pm 150$ V power supply. This provided the amplitude of the “ion shutter” pulse. The ion shutter was triggered by a TTL pulse from a Farnell pulse delay generator, which was in turn triggered by the first pulse from a LeCroy pulse delay generator which

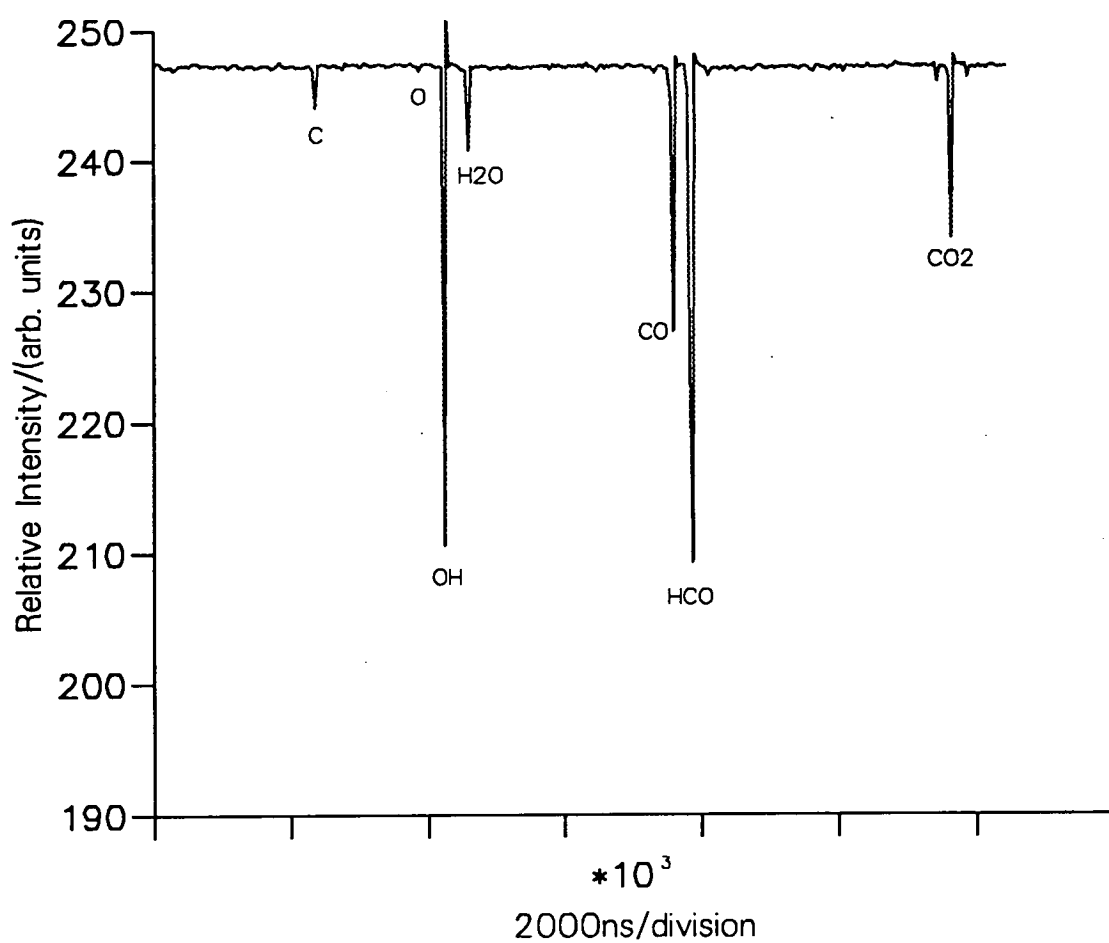


Figure 3-3: Time-of-flight mass spectrum showing the main products from the photolysis of formic acid. The UV laser power was 1 mJ per pulse and the focal length lens used was 6 cm.

initiated the whole of the experimental cycle. The Farnell pulse delay generator was used to control the width and delay of the final output ion shutter pulse.

Ideally the ion shutter should be able to shutter out ions 1 amu apart. However, the risetime of the final output pulse was $\sim 1\mu\text{s}$, which meant that only ions ≥ 3 amu apart could be separated. This was satisfactory for our present purposes.

It is possible to use a pulsed grid as a shutter rather than a plate[14]. A plate is preferable because the ion trajectories are very sensitive to the voltage on the plate, and there is little "leakage" when the shutter is closed. In addition all grids have transmission losses.

Figure 3-4 demonstrates the successful application of the ion shutter. The top panel shows the TOF spectrum obtained through the photolysis/probe of formic acid with the ion shutter switched off. The bottom panel was obtained under the same experimental conditions with a -30 V, $100\mu\text{s}$ pulse delayed by $6.5\mu\text{s}$ from the laser, applied to the horizontal deflection plates. It can be seen that the pulse has been effective in removing the non-resonant CO and HCO mass peaks.

Wavelength Scans: The $D^2\Sigma^-$ and $3^2\Sigma^-$ states.

A (2+1) REMPI spectrum of the $D^2\Sigma^-(v'=0) \leftarrow X^2\Pi(v''=0)$ band is shown in figure 3-5.

This spectrum closely resembles the spectrum obtained by de Lange *et al* [1] and shows the $Q_1(1)$ and $Q_2(1)$ lines have almost the same intensities as the O, P, R and S branches, but decrease rapidly as N'' increases. The O, P, R and S branches can be traced up to only $N'' = 6$ which reflects a low rotational temperature. These results agree with the original ones obtained by Ebata *et al*[15] in which the internal state distributions of OH were measured by LIF following photolysis of formic acid at 246 nm. They found the OH fragment to be vibrationally and rotationally cold (only $v'' = 0$ was populated up to $N'' = 5$).

Attempts were made to try and increase the signal to noise ratio for the spectrum shown in figure 3-5 by changing to a shorter focal length focusing lens (3 cm) and increasing the pressure of formic acid within the reaction chamber. Neither of these measures made any significant gains.

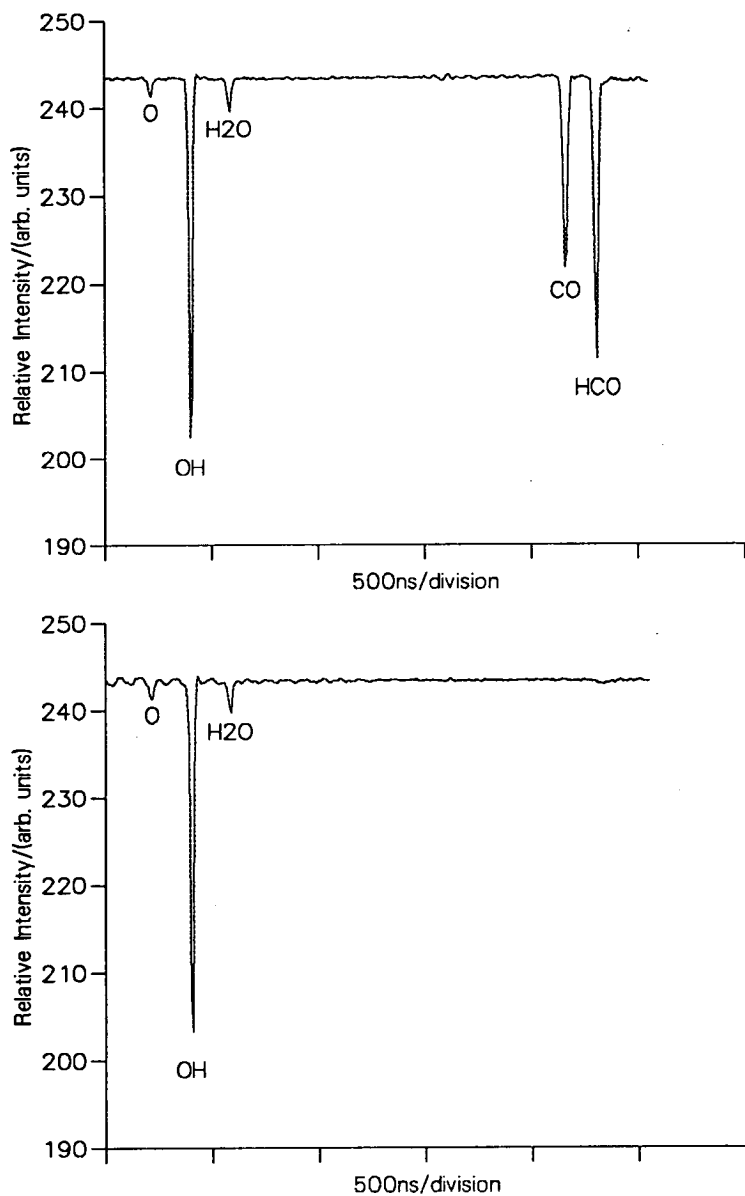


Figure 3-4: The top panel shows part of the time-of-flight mass spectrum obtained from the photolysis of formic acid. The bottom panel mass spectrum was taken under the same experimental conditions with the ion shutter applied to remove the non-resonant CO and HCO peaks.

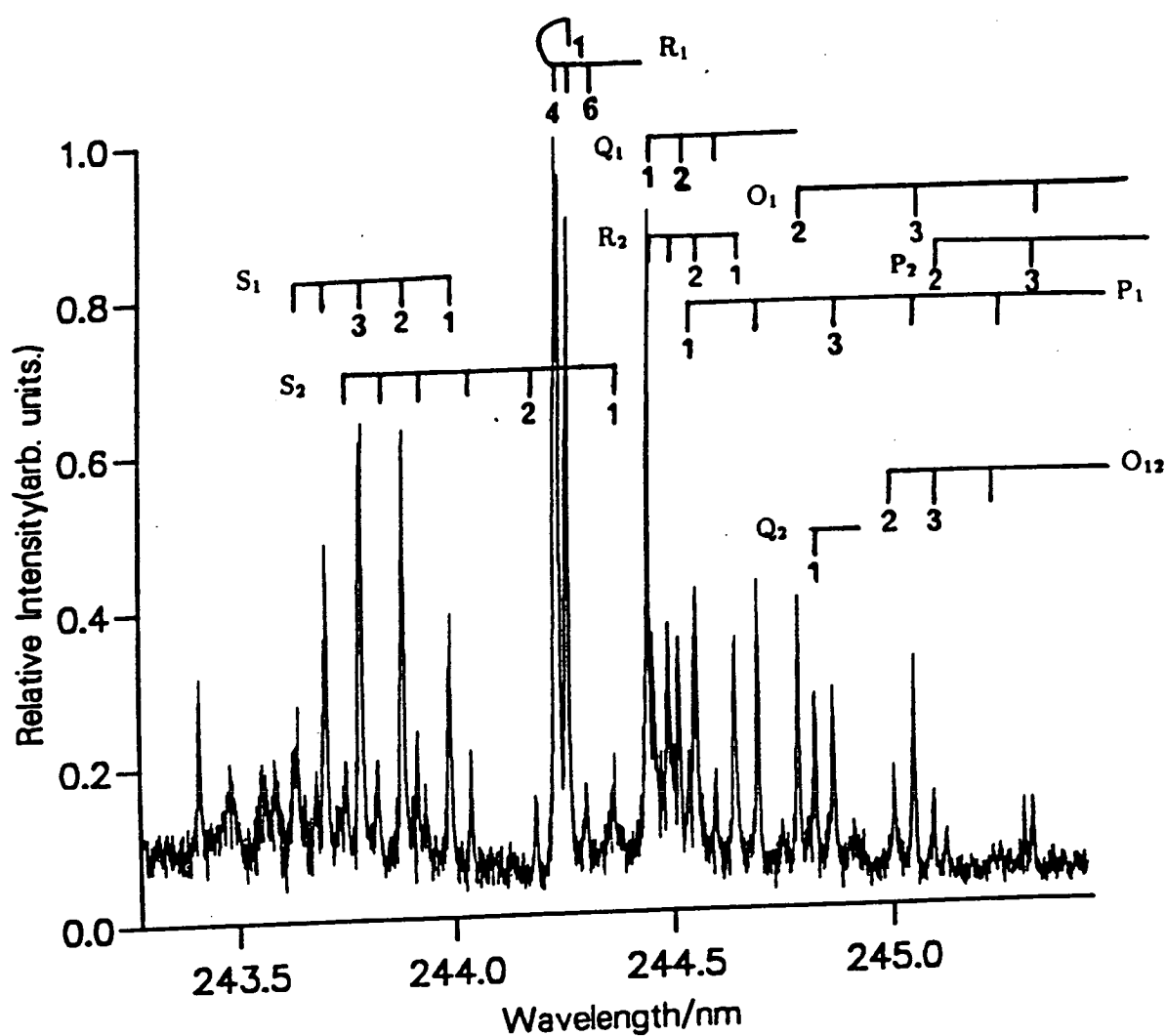


Figure 3-5: (2+1) REMPI spectrum of the $D^2\Sigma^-(v'=0) \leftarrow X^2\Pi(v''=0)$ band of OH produced from photodissociation of formic acid.

Figure 3-6 shows the (2+1) REMPI spectrum of the $3^2\Sigma^-(v'=0) \leftarrow X^2\Pi(v''=0)$ band. Again only rotational levels up to $N''=6$ are shown to be populated. The signal to noise ratio for the $3^2\Sigma^-(v'=0) \leftarrow X^2\Pi(v''=0)$ band is clearly better than that for the $D^2\Sigma^-(v'=0) \leftarrow X^2\Pi(v''=0)$ band. The extinction coefficient for formic acid at 244.44 nm (which corresponds to the Q_1 line of the D-X(0-0) band) is $2 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$, whereas at 227.95 nm (which corresponds to the Q_1 line of the 3-X(0-0) band) is $30 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$. Therefore, assuming the same laser intensity and beam radius were used for both transitions, we should expect to dissociate approximately fifteen times more formic acid molecules for the 3-X(0-0) band than for the D-X(0-0) band. This may partly explain the better signal to noise ratio for the 3-X(0-0) band.

3.4.2 $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$

In this section we hoped to eliminate the wavelength dependence of the OH source by generating the OH radical via the $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$ reaction. Extremely intense NO signals, from either the product of the reaction or from contamination of the NO_2 cylinder, were pulsed out, using the ion shutter described above, allowing the detector to be set at the higher levels required for the detection of OH.

Unfortunately, although we did observe evidence of production of OH radicals from the reaction (monitored via the $3^2\Sigma^-(v'=0) \leftarrow X^2\Pi(v''=0)$ band) the signal to noise ratio was too poor to run a spectrum. The OH REMPI signal required flows of both H_2 and NO_2 , proving that it originated from the reaction and not from the photolysis of contaminant formic acid within the reaction chamber. The experiment was principally restricted by the pressure allowed at the laser focus region. Increasing the flows of both H_2 and NO_2 should increase the number of OH radicals generated. However, the short focal length focusing lens used created too high ion densities of ions such as NO^+ etc., leading to space charging which limited the efficiency with which the resonantly produced OH^+ ions could be extracted from the reaction region to the detector.

A severe limitation of using REMPI to probe nascent OH radicals from a hot atom dynamics type experiment may be that the high probe laser powers needed

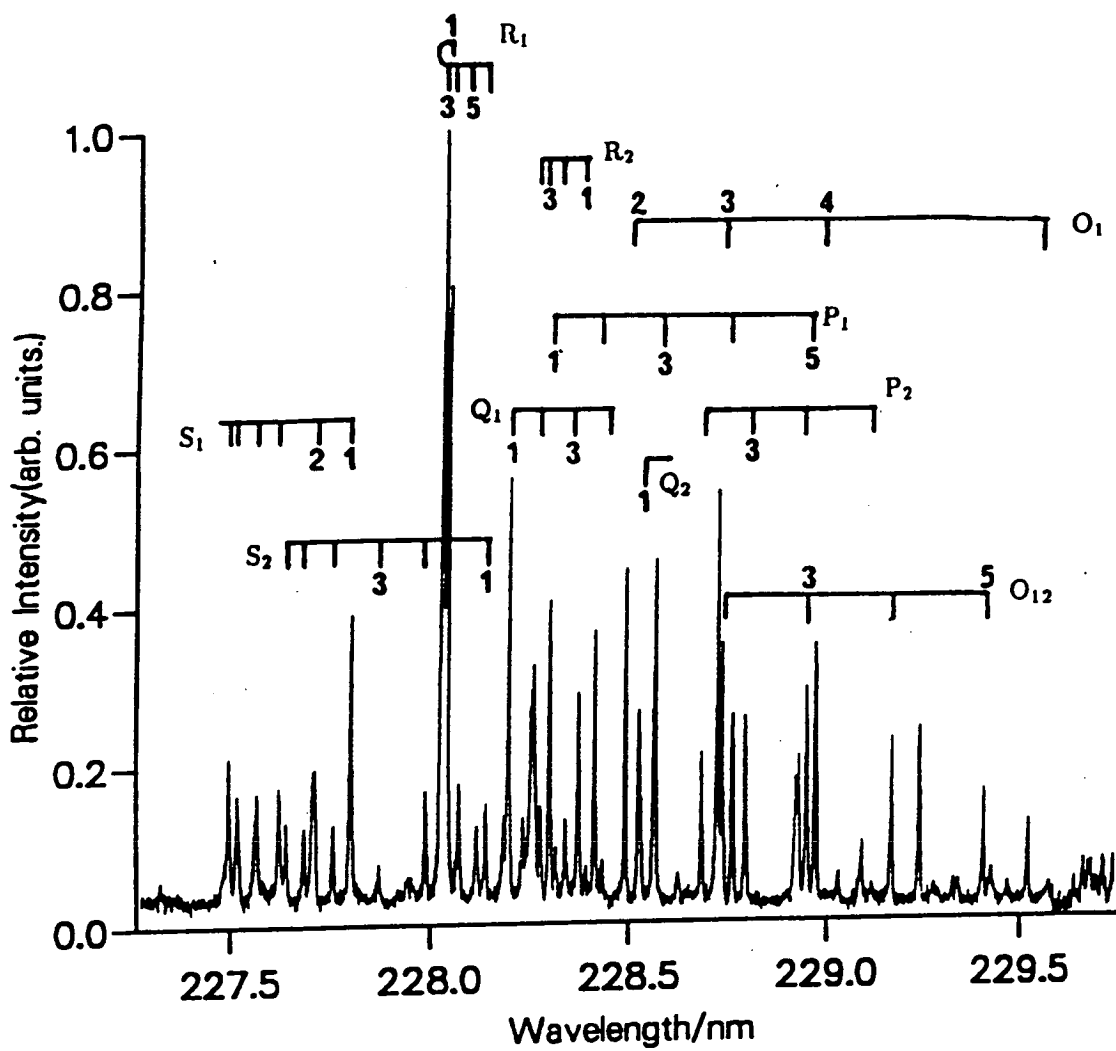


Figure 3-6: (2+1) REMPI spectrum of the $3^2\Sigma^-(v'=0) \leftarrow X^2\Pi(v''=0)$ band of OH produced from photodissociation of formic acid

for OH detection, may induce unwanted photolysis and ionisation of reagents and precursors leading to a high density of non-resonant ions. Because of this anticipated problem we decided to carry out some more preliminary experiments probing the OH radical by laser induced fluorescence. The merits of both detection methods could then be compared before deciding on which method would be best employed for a hot atom dynamics experiment producing OH as a nascent reaction product.

3.5 LIF Spectroscopy of the OH Radical

As discussed in the introduction to this chapter the most widely used method of detecting the hydroxyl radical is by laser-induced fluorescence via the one-photon $A^2\Sigma^+ \leftarrow X^2\Pi$ transition.

The rotational selection rules for a one-photon transition are $\Delta J = 0, \pm 1$. For pure Hund's case (b) the selection rules are $\Delta N = 0, \pm 1$. In Hund's case (a) the quantum number N is not defined and hence the selection rules for ΔN do not hold. Transitions between $^2\Pi$ and $^2\Sigma^+$ states satisfying both ΔJ and ΔN selection rules give rise to 12 branches. These are shown in figure 3-7.

3.5.1 Experimental Procedure

The main apparatus used to do an LIF experiment was described in section 2.3. The reader is referred back to figure 2-4 which shows a schematic of the apparatus used for LIF detection. What follows is a brief summary of the procedure pertinent to this particular experiment.

The OH radical was generated via the microwave discharge of water in a quartz glass tube external to the vacuum chamber. The water vapour was admitted through the quartz discharge tube by letting a stream of an oxygen/argon mixture (1:1) flow over a reservoir of water upstream of the discharge region. The discharge tube terminated in a 1-mm orifice through which the gases expanded to form an effusive jet. The injector tip was located 25 mm from the centre of the region

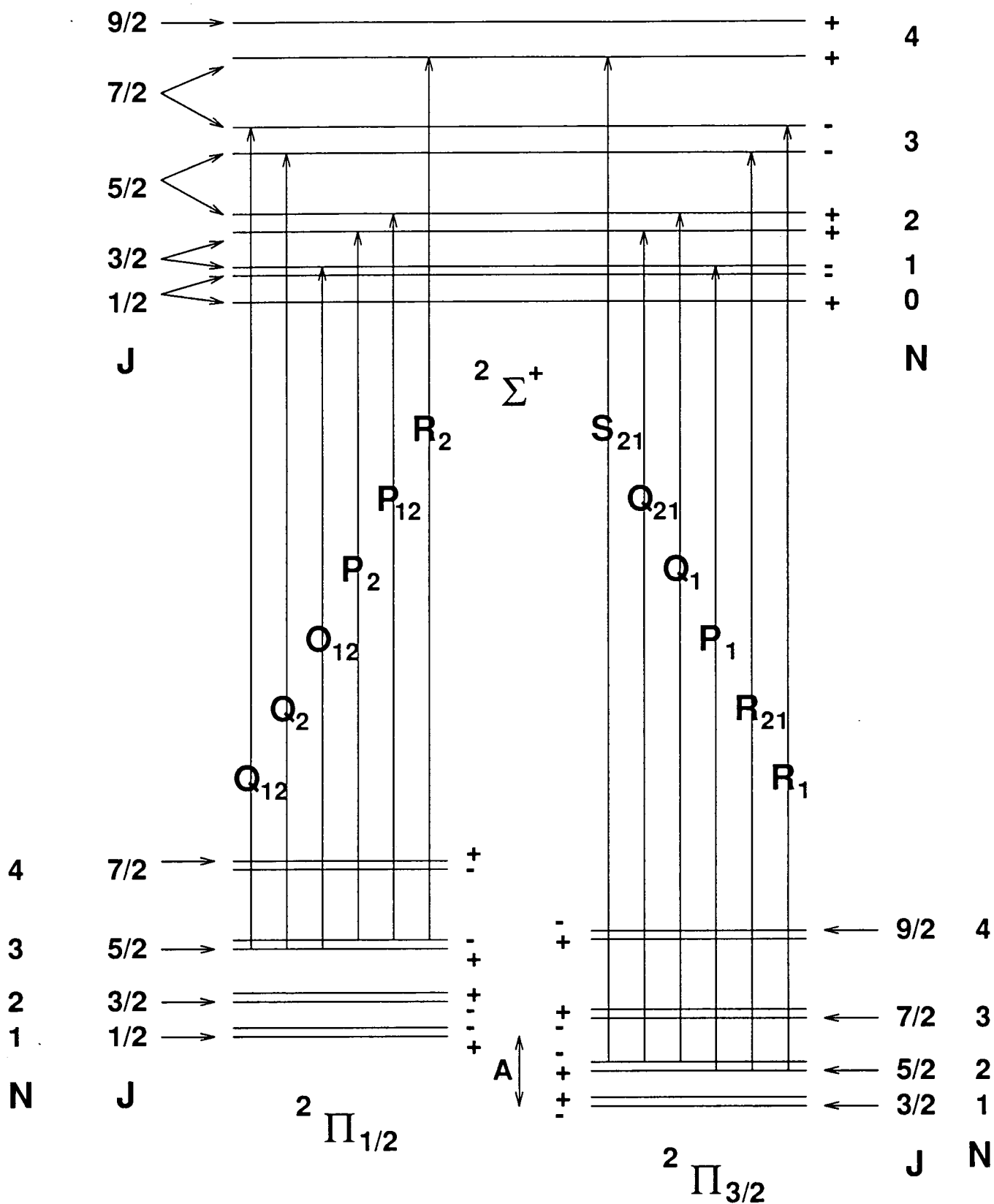


Figure 3–7: Energy level diagram for $2\Sigma^+ (b) \leftarrow 2\Pi(a)$ transition. The Π state levels are split into two widely separated stacks due to spin-orbit splitting into the $2\Pi_{1/2}$ and $2\Pi_{3/2}$ states, which are inverted for OH. Branches are labelled according to Hund's case (a). In the $2\Sigma^+$ state levels with the same N are split into $J=N\pm 1/2$ by the spin-rotation interaction.

probed by the LIF excitation beam. Typical pressures in the reaction chamber were ~ 50 mTorr.

Laser-induced fluorescence was excited by tunable ultraviolet radiation, produced by frequency-doubling the output of the dye laser. Output energies from the doubled dye beam were ~ 3 mJ which is far in excess of the energy required to excite fluorescence in OH. The laser power was reduced by using a pair of Glan-Taylor prisms which allowed variable attenuation of the probe beam while maintaining a fixed linear polarisation axis.

Fluorescence was detected in the vertical direction, perpendicular to the laser beam axis. A combination of fused silica lenses imaged the fluorescence through a suitable interference filter, chosen to transmit radiation at the wavelength of the desired OH $A^2\Sigma^+ \leftarrow X^2\Pi$ vibronic transition, onto the photocathode of the photomultiplier tube. Signals were captured during a $1.5\mu\text{s}$ gate (corresponding to approximately twice the OH $A^2\Sigma^+ \leftarrow X^2\Pi$ fluorescence lifetime), delayed ~ 20 ns from the probe pulse to discriminate against scattered light.

3.5.2 Results and Discussion

Figure 3-8 shows the LIF excitation spectrum of the OH $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=0)$ band. Fluorescence was selectively detected on the (1,1) band. This spectrum was obtained at a pressure of 35 mTorr with a laser energy of $350\mu\text{J}$ around 282 nm. The rotational lines are thermally populated as expected. The lines are slightly broadened above the instrumental laser linewidth indicating that they have been saturated at the laser energy used (a careful study of the effects of radiative saturation in the LIF of OH was left until chapter 4).

A direct comparison of LIF versus REMPI for OH would require an estimation of the concentration of OH radicals produced by either photolysis or microwave discharge, as well as a detailed knowledge of the rotational line strengths for the LIF and REMPI processes. We did not have time for such a detailed study. We rather tried to acquire a qualitative sense of the relative detection efficiencies of LIF compared to REMPI.

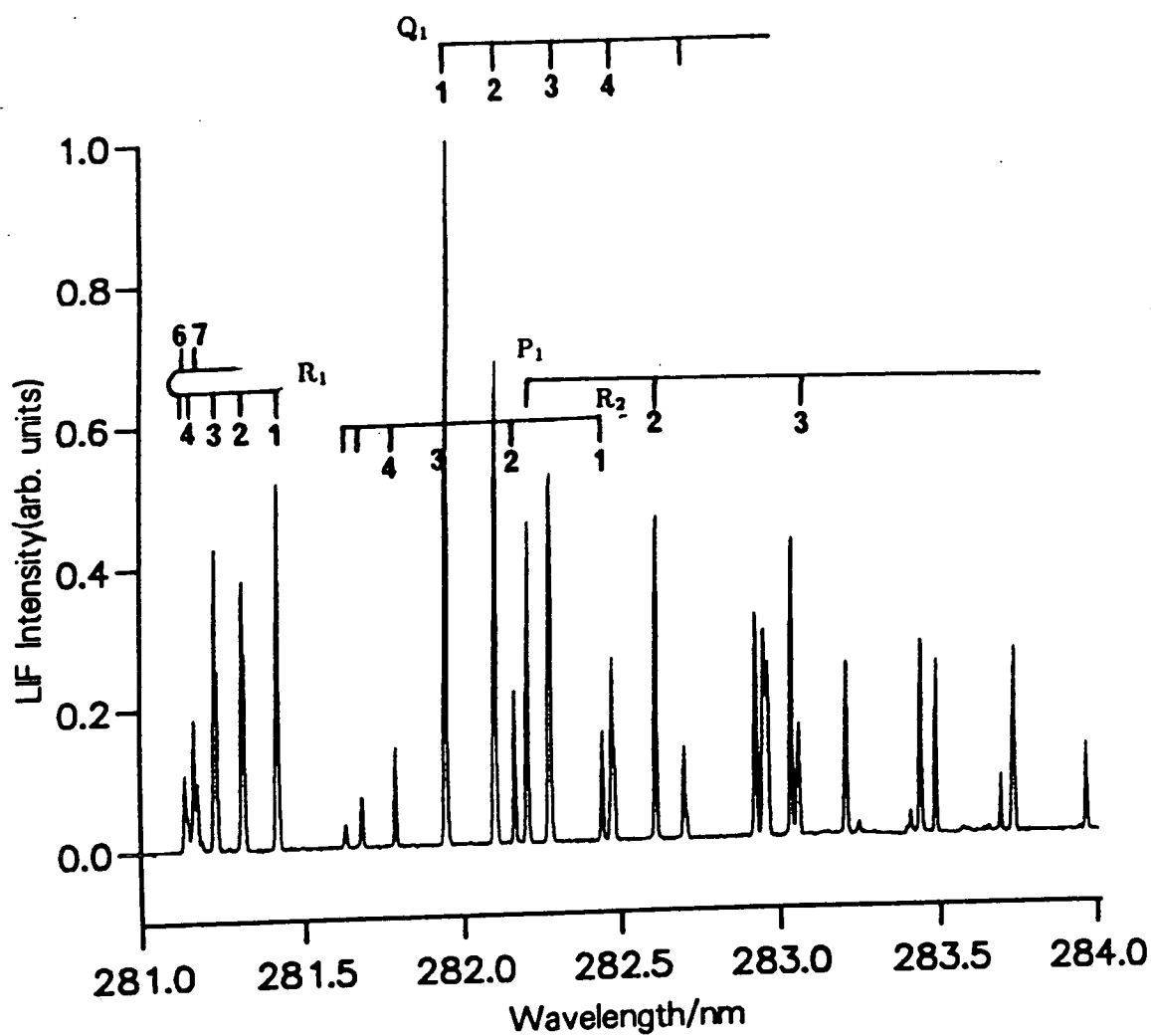


Figure 3-8: LIF excitation spectrum of the OH $A^2\Sigma^+(v'=1) \leftarrow X^2\Pi(v''=0)$ band from the microwave discharge of water. Fluorescence was selectively detected on the (1,1) band.

The signal to noise ratio shown in figure 3-8 is far better than that achieved for either of the REMPI transitions studied. At this point several factors started to sway us towards using LIF rather than REMPI to detect OH produced in a dynamical experiment.

The concentration of nascent product molecules formed in a hot atom dynamics experiment is dependent (among other factors) on the pressures of the constituent reactants. The pressure constraints set by the microchannel plate detector in a REMPI experiment limits the ability to detect the small quantities of nascent product molecules formed. This is not a problem in an LIF experiment since the detector is external to the vacuum chamber. Initially, large pressures can be used to find a signal from a bimolecular reaction, after which other optimisation procedures can be carried out so that the total pressure can be reduced, thus ensuring the true nascent character of the reaction products is observed.

The short focal length lens required for REMPI detection of OH may also introduce practical problems in a hot atom dynamics experiment, since the much increased intensities created may lead to unwanted probe- induced photolysis and ionisation of the reactants.

From a theoretical standpoint converting measured intensities to populations is significantly more complicated for REMPI than for LIF. The one-photon absorption rotational linestrength formulae and selection rules applied to OH are extremely well known[2] and have been used in numerous reaction dynamics studies. Although the rotational linestrength formulae for a 2-photon absorption process for states belonging to Hund's case (a) have been used frequently, less well used are the two-photon rotational linestrength formulae for transitions involving states of differing Hund's case coupling, as in OH. This arises from the combined complexity of spin-orbit splitting with the added number of possible transition pathways allowed via two photon absorption.

All of the above reasons led us to choose LIF detection of OH for the hot atom dynamics experiments attempted in chapter 4.

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Chapter 4

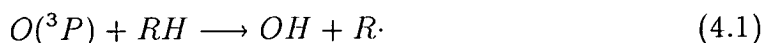
Bimolecular Reaction Dynamics

The reactions of $O(^3P)$ with simple organic molecules are of considerable practical importance, particularly through their involvement in combustion and atmospheric chemistry. Because of this, there have been literally hundreds of measurements of thermal rate constants for these reactions for use in kinetic models[1].

The dynamics of these processes were first investigated by Andresen, Luntz and Kleiner, who combined the crossed molecular beam technique with laser-induced fluorescence as a means of determining the product OH internal state distributions. They studied the reactions of $O(^3P)$ with saturated[2] and unsaturated[3] hydrocarbons, amines[4] and aldehydes[5]. Whitehead's group has investigated the reactions of $O(^3P)$ with benzene[6] and ethanol[7] using the same techniques as Luntz *et al.*

The aim of this chapter was to reinvestigate some of the reactions of $O(^3P)$ with various hydrocarbons by the alternative hot atom dynamics technique discussed in chapter 1. Briefly, $O(^3P)$ atoms were produced via laser photolysis of a suitable precursor molecule in the presence of a saturated hydrocarbon molecule. An independent tunable pulsed laser system was then used for the state-specific spectroscopic detection of products. The time delay between photolysis and probe could be adjusted to ensure that genuinely nascent product state distributions were observed, from which the dynamics of the reaction may be hopefully inferred. Following the findings of chapter 3, we opted to detect the OH product by LIF via the $A^2\Sigma^+ \leftarrow X^2\Pi$ electronic transition.

The mechanism that is usually assumed for the reaction of $O(^3P)$ with saturated hydrocarbons RH is a simple hydrogen abstraction i.e.



where $R\cdot$ is an alkyl radical. For $O(^3P)$ abstraction in saturated hydrocarbons, it is necessary to distinguish three types of C-H bonds: primary (RCH_3), secondary (R_2CH_2), and tertiary (R_3CH). This classification is necessary because the various C-H bonds have different bond strengths, i.e., ~ 420 , ~ 397 and ~ 385 kJ mole^{-1} for primary, secondary and tertiary bonds, respectively[8]. This produces both different reaction energetics and kinetics in the three cases. The results are summarised in the correlation diagrams shown in figure 4-1, which are one-dimensional representations of the potential energy surfaces for abstraction in each case.

All the reactions are slightly exothermic with $\Delta H_0 = -9.62$, -30.1 and -43.1 kJ mole^{-1} for primary, secondary and tertiary abstraction, respectively[8]. The barriers to reaction vary substantially in the series and are ~ 28.9 , ~ 18.8 , and ~ 13.8 kJ mole^{-1} , respectively[2]. Activation energies do depend significantly on the type of C-H bond abstracted, but are otherwise independent of the exact nature or complexity of the hydrocarbon reactant which suggests that the reactions involve strong interaction of $O(^3P)$ with only the individual C-H bonds, rather than with the entire hydrocarbon molecule simultaneously.

Significant reactive cross sections are only obtained at collision energies higher than the activation energy barrier. These are achievable in molecular beam experiments since the initial collision energy between the reactants can be substantially increased and controlled through the beam velocities. As the name suggests it is also possible in hot atom dynamics experiments where the collision energy can be chosen by photolysing different precursor molecules (containing the photofragment of interest) at different wavelengths.

A logical series of experiments was devised so as to have the best chance of achieving the aim of this chapter. These experiments essentially started with the work of chapter 3 which established that LIF remained the optimum method for the detection of OH under our reaction conditions. The next experiment was aimed at proving that we could generate a source of $O(^3P)$ atoms via the photolysis of

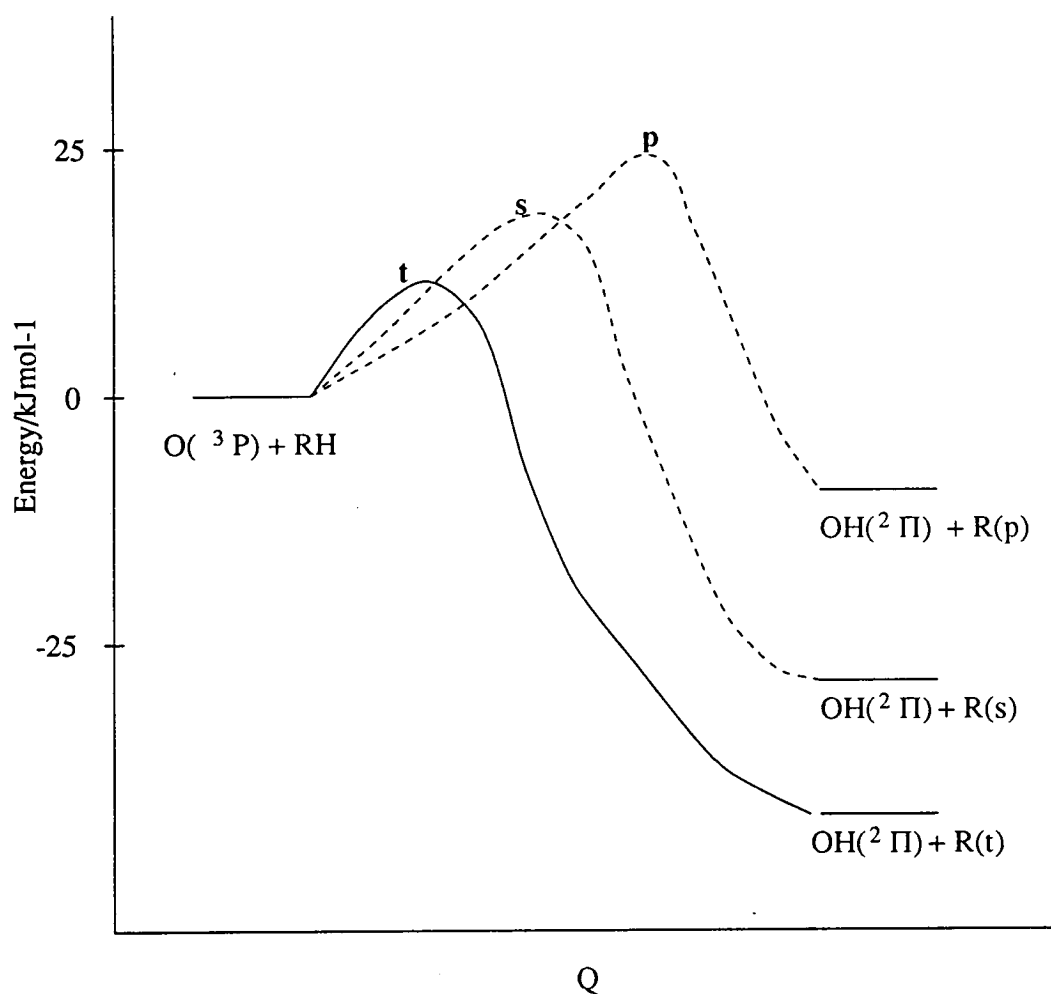


Figure 4-1: Schematic correlation diagrams for the reactions of $\text{O}(^3\text{P})$ with saturated hydrocarbons. Q is the reaction coordinate. The curves are labelled p, s and t to represent abstraction of primary, secondary and tertiary hydrogens, respectively. This diagram was taken from reference [2].

NO₂. This simple photolysis/probe type experiment served as a good prerequisite to the more difficult photolysis/reaction/probe experiment to be attempted.

4.1 The Photolysis of NO₂.

Nitrogen dioxide is known to photodissociate by absorption of UV light below 397.8nm to produce NO(²Π_Ω; *v*" , *J*") and O(³P_{*J*})[9], where *v*" and *J*" represent the vibrational and rotational quantum numbers of NO, and the spin-orbit states of NO are denoted by Ω(=1/2 or 3/2) and those of O by *J*(=0,1 or 2).

The first investigation of the internal energy distributions in the fragments formed from the photolysis of NO₂ was performed by Busch and Wilson[10], using time-of-flight photofragmentation spectroscopy. Their experiments reported the formation of both NO (*v*" = 0) and (*v*" = 1) fragments formed at a photolysis wavelength of 347.1 nm.

Zacharias, Welge and co-workers[11] reported the first well-resolved NO vibrational and rotational state distributions following 337, 308, and 351 nm photolysis of NO₂ using one-photon LIF for probing NO directly. Mons and Dimicoli[12] employed REMPI-TOF probing of NO(*v*" = 1) and studied the photolysis of NO₂ at several wavelengths close to the NO(*v*" = 1) threshold between 379 and 348 nm.

The vibrational distributions of the NO photofragment observed so far have been nonstatistical, favouring formation of vibrationally excited NO. The rotational distributions on the other hand appear to be in better accord with statistical calculations. All of the above studies were carried out with room temperature samples of NO₂. More recently, Pfab and co-workers[13] have investigated the effects of jet cooling of the NO₂ on the rotational distributions of the NO(*v*" = 1) fragment. They have found strong deviations from statistical predictions for the rotational distributions.

The internal state distributions of the O(³P_{*J*}) product have also been determined following the photolysis of NO₂ at various photolysis wavelengths. For the oxygen atom , ³P₂ is the lowest-lying multiplet, ³P₁ lies 158.5 cm⁻¹ above ³P₂,

and $^3P_0$ lies 68.0 cm^{-1} above $^3P_1$ [17]. Tunable UV and VUV lasers make the interrogation of the ^3P_J levels possible. Several different methods have been used up to now. Miyawaki *et al*[15] have used 1-photon LIF via the $3s^3S_J \leftarrow 2p^3P_J$ transition at 130 nm, following the photolysis of NO_2 at 355 nm, 337 nm and 266 nm. They found the $\text{O}(^3P_J)$ distributions produced to be essentially the same for the three different photolysis wavelengths, these were measured to be $^3P_2: ^3P_1: ^3P_0$ 1:0.19:0.03. Zare[16], also using LIF, monitored the populations via the 2-photon $3p^3P_J \leftarrow 2p^3P_J$ transition at 226 nm after photolysing NO_2 at 355 nm. Their measured $\text{O}(^3P_J)$ distributions were in excellent agreement with Miyawaki[15]. Zare also listed the distributions expected for a purely statistical distribution of $\text{O}(^3P_J)$ states, these were $^3P_2: ^3P_1: ^3P_0$ 1:0.60:0.20. Matsumi[17] has used (2+1) REMPI via the $3p^3P_J \leftarrow 2p^3P_J$ transition to monitor the $\text{O}(^3P)$ spin-orbit populations following the photolysis of O_2 at 157 nm..

We had essentially three convenient options for monitoring the photolysis of NO_2

1. monitor the production of $\text{O}(^3P)$ atoms directly via the (2+1) REMPI $3p^3P_J \leftarrow 2p^3P_J$ transition.
2. monitor the production of the $\text{NO}(v'' = 0)$ photofragment via the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi_{1/2}(v''=0)$ transition, either by LIF or (1+1) REMPI.
3. monitor the production of the $\text{NO}(v'' = 1)$ photofragment via the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi_{1/2}(v''=1)$ transition (by LIF or REMPI).

The first option would require a short focal length focusing lens to create the high laser intensities required to drive a 2-photon resonant process. It was anticipated that the high laser intensities produced could lead to unwanted probe induced photolysis.

The second option would involve probing the $\text{NO}(v'' = 0)$ photofragment via LIF or (1+1) REMPI. This transition is extremely intense and does not require a focusing lens. At the time our apparatus was configured for REMPI detection, and it was therefore more convenient to use this technique rather than LIF. A (1+1) REMPI spectrum of this transition is shown in figure 4-2. This spectrum

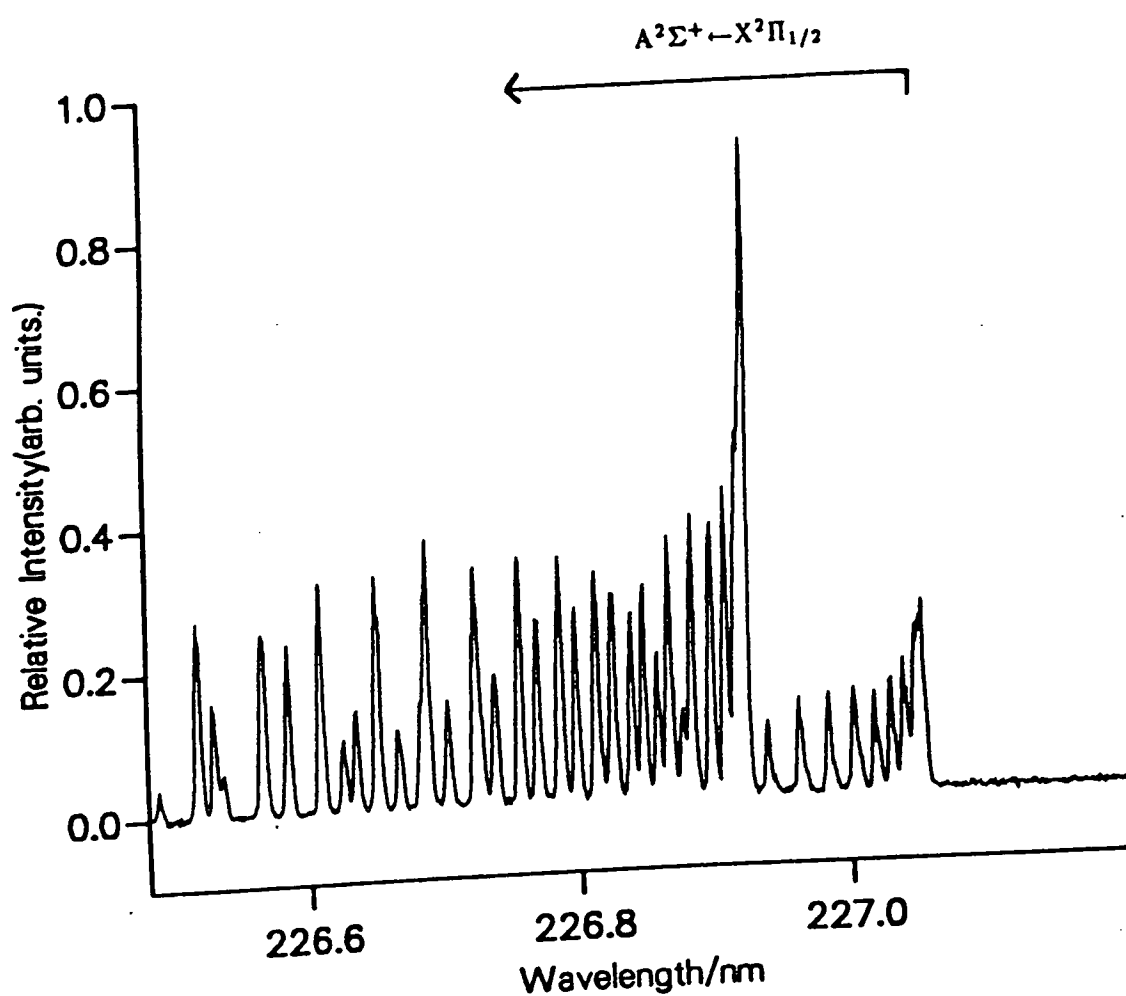


Figure 4-2: The (1+1) REMPI $A^2\Sigma(v'=0) \leftarrow X^2\Pi_{1/2}(v''=0)$ vibronic band of NO. This spectrum was recorded with the probe laser only and results from the NO contaminant in an NO_2 sample at a total pressure of 1×10^{-5} mbar.

was recorded with a pressure 1×10^{-5} mbar of NO_2 with the photolysis laser off i.e. the source of NO was just contaminant NO from the NO_2 cylinder. The large signal to noise ratio shown in this spectrum demonstrates the ease of detection of $\text{NO}(v'' = 0)$, however it also illustrates the problem of trying to distinguish between $\text{NO}(v'' = 0)$ produced by the photolysis of NO_2 and just background NO.

We chose to focus our attention on the third option since, (a) the detection of $\text{NO}(v'' = 1)$ is also a (1+1) REMPI process, reducing the possibility of any probe induced photolysis and (b) the fraction of $\text{NO}(v'' = 1)$ in a sample of NO_2 is negligible meaning that the $\text{NO}(v'' = 1)$ produced would be virtually exclusive to the photolysis of NO_2 .

4.1.1 Experimental

The equipment required to carry out a photolysis/probe type experiment was described in section 2.5.2. The reader is referred back to figure 2-8 which shows a schematic diagram of the apparatus.

NO_2 gas was admitted into the reaction chamber through the back flange. This resulted in a pressure of typically 1×10^{-4} mbar in the chamber. The output from the photolysis laser (337nm, 5mJ per pulse) was loosely focused by a 30 cm focal length quartz lens to a rectangularly shaped spot size (10 mm $\times$ 5 mm) located at the centre of the chamber. After an electronically controlled delay, the unfocused probe beam (200 μ J per pulse) propagated along the same axis in the opposite direction to induce the $\text{NO}(v'' = 1)$ detection process. The $\text{NO}(v'' = 1)$ photofragment was probed via the (1+1) REMPI $A^2\Sigma^+ \leftarrow X^2\Pi$ transition on the (0-1) vibronic band. Ions of $m/e = 30$ were selectively detected by TOF.

Concurrent spectra could be recorded under the same experimental conditions, at different time delays, Δt , between the firing of the two lasers, using the data acquisition facilities discussed in section 2.6.10.

4.1.2 Results and Discussion

The lower panel of figure 4-3 shows a spectrum over the wavelength region where the $A^2\Sigma^+ (v'=0) \leftarrow X^2\Pi_{3/2}(v''=1)$ vibronic band is expected. This spectrum was recorded at a NO_2 pressure of 1×10^{-4} mbar with the probe laser beam only. The small amount of signal present is attributed to thermal $\text{NO}(v''=1)$ in the NO_2 sample. The upper panel shows a spectrum of the same transition with both lasers firing. This spectrum was recorded under the same conditions as the top panel spectrum with no time delay between the photolysis and probe lasers and shows the many rotational lines of the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi_{3/2}(v''=1)$ vibronic band. The higher rotational levels are generally located towards the low wavelength region of the spectrum. No attempt has been made to properly analyse these spectra since, as discussed, many research groups have already investigated the detailed dynamics of the photodissociation of NO_2 . We merely wanted to verify that $\text{O}(^3\text{P})$ was being produced via the laser photolysis of NO_2 .

Further verification of the proper operation of the apparatus is shown in figure 4-4. Again the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi_{3/2}(v''=1)$ vibronic band was recorded following the photodissociation of NO_2 . The two spectra shown were recorded simultaneously for different Δt 's and the rotational distributions obtained are clearly different. The top panel spectrum was recorded with $\Delta t = 0$ ns and shows the lower rotational levels to be relatively more populated. The lower panel spectrum was recorded with $\Delta t = 3\mu$ s and shows the higher rotational levels to be populated as much as the lower levels indicating a rotationally hotter distribution. This can be explained by the fact that since the total energy available in the photolysis process is fixed then the $\text{NO}(v''=1)$ products formed in higher rotational levels will carry less energy in translation and will therefore remain in the probe observation region for a longer period. Consequently, at the longer photolysis/probe delay time a relatively higher concentration of rotationally hot, translationally cold $\text{NO}(v''=1)$ products remain in the probe observation region, whereas most of the $\text{NO}(v''=1)$ products formed in the lower rotational levels (which have more translational energy) will have flown out of the observation region before having a chance of being probed.

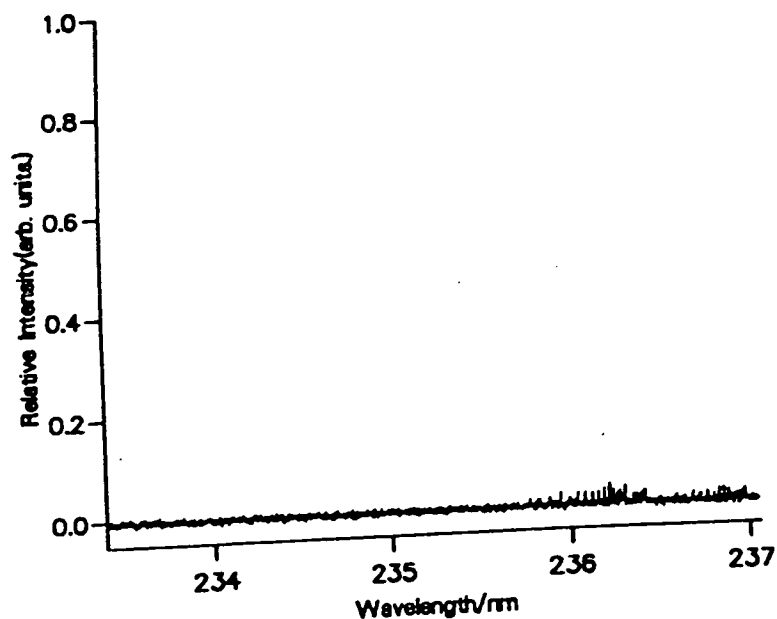
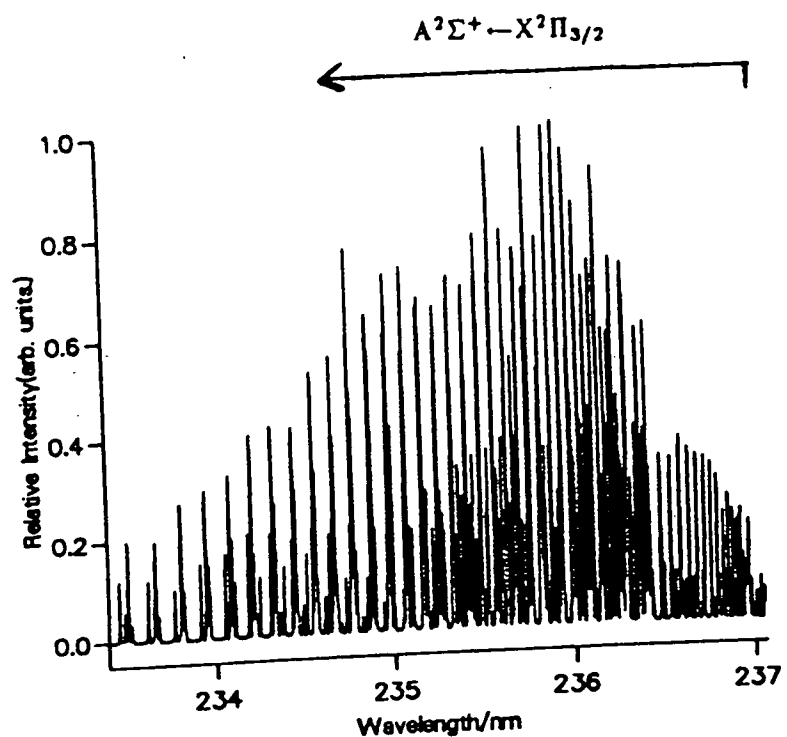


Figure 4-3: The upper panel shows a spectrum of the (1+1) REMPI $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi_{3/2}(v''=1)$ vibronic band produced by the 337 nm photolysis of NO_2 . The lower panel shows a background spectrum recorded under the same experimental conditions, without the photolysis laser firing.

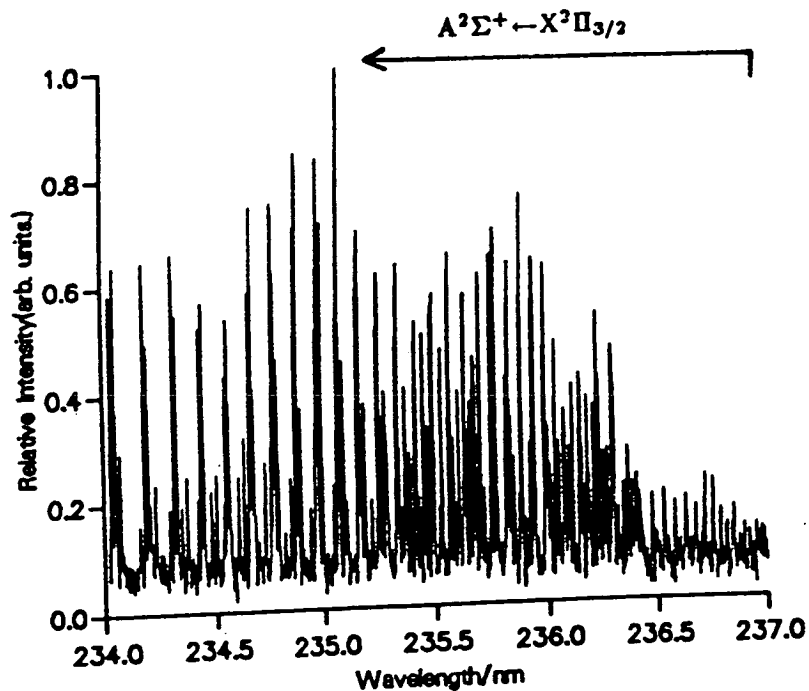
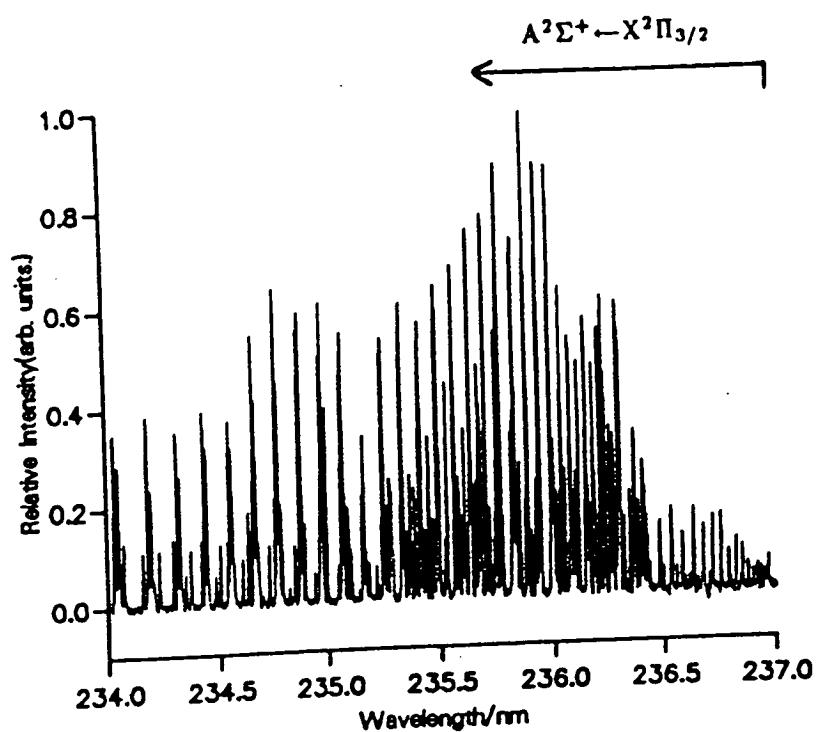


Figure 4-4: Both of the above spectra show the (1+1) REMPI $A^2\Sigma^+(v' = 0) \leftarrow X^2\Pi_{3/2}(v''=1)$ vibronic band of NO. The NO was produced via the 1-photon, 337 nm photolysis of NO_2 . The upper panel spectrum was taken with no time delay between photolysis and probe lasers, whereas the lower panel spectrum was taken with a time delay of $3\mu\text{s}$.

4.2 O(³P) + RH Reactions

Having established a reliable photolytic source of O(³P) atoms we then proceeded with the main task of attempting to evaluate the product state distributions from the reaction of these atoms with various hydrocarbons using the hot atom dynamics technique.

4.2.1 Reaction Energetics

Ethane, cyclohexane and isobutane were chosen to represent primary, secondary and tertiary hydrocarbons, respectively (where it is implicitly assumed that in the isobutane case the observed products are dominated by abstraction of the hydrogen atom attached to the weakest, tertiary C-H bond). As discussed above, different C-H bond strengths lead to different reaction exothermicities. The total available energy is the sum of the reaction exothermicity and the internal and translational energies of the reagents. Figures 4-5 to 4-7 present diagrams showing relative energies of reagent and product states for each of the different type of hydrocarbon. Chapter 1 discussed how the thermal motions of the reagents in a hot atom dynamics experiment leads to a spread in the relative collision energy. An analytical expression was derived which quantified the distribution of collision energies (see appendix A, equation A-7). Using this expression, plots of the collision energy distributions for each of the O(³P) + hydrocarbon reactions, at each of the photolysis wavelengths, were constructed and are shown in figures 4-8 and 4-9. The mean collision energy and it's associated thermal spread for each reaction are summarised in table 4-1. It should be noted that the spread shown is only the thermal spread and there is an additional spread caused by the distribution of possible NO states produced in the photolysis of NO₂. No attempt has been made to quantify this spread.

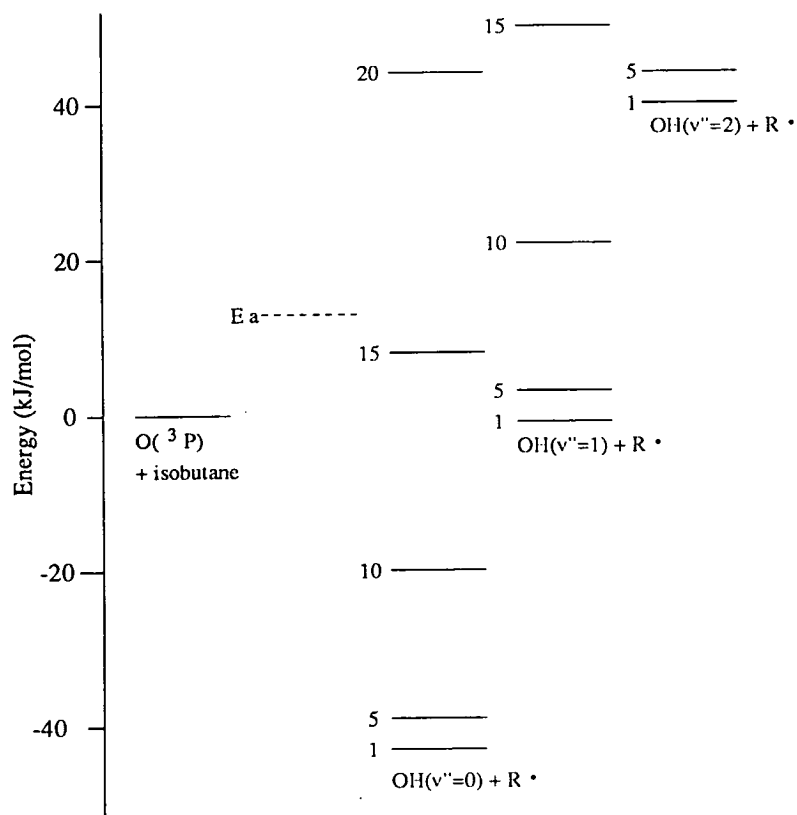


Figure 4–5: Energetics for the $\text{O}(^3\text{P}) + \text{iso-C}_4\text{H}_{10} \rightarrow \text{OH}(X^2\Pi_{3/2}) + \text{C}_4\text{H}_9$ reaction system. E_a is the activation barrier and the numbering of the rotational levels, N'' , are indicated.

$\text{O}(^3\text{P}) + \text{RH}$	$\lambda_{\text{phot}}/\text{nm}$	$E_{\text{colln}}/\text{kJ mol}^{-1}$
ethane	337	25.2 ± 19.1
ethane	308	39.4 ± 24.2
cyclohexane	337	31.4 ± 19.3
cyclohexane	308	49.7 ± 24.5
isobutane	337	29.6 ± 19.4
isobutane	308	46.6 ± 24.6

Table 4–1: Calculated average collision energies for 300 K reagents and precursor. λ_{phot} is the photolysis wavelength.

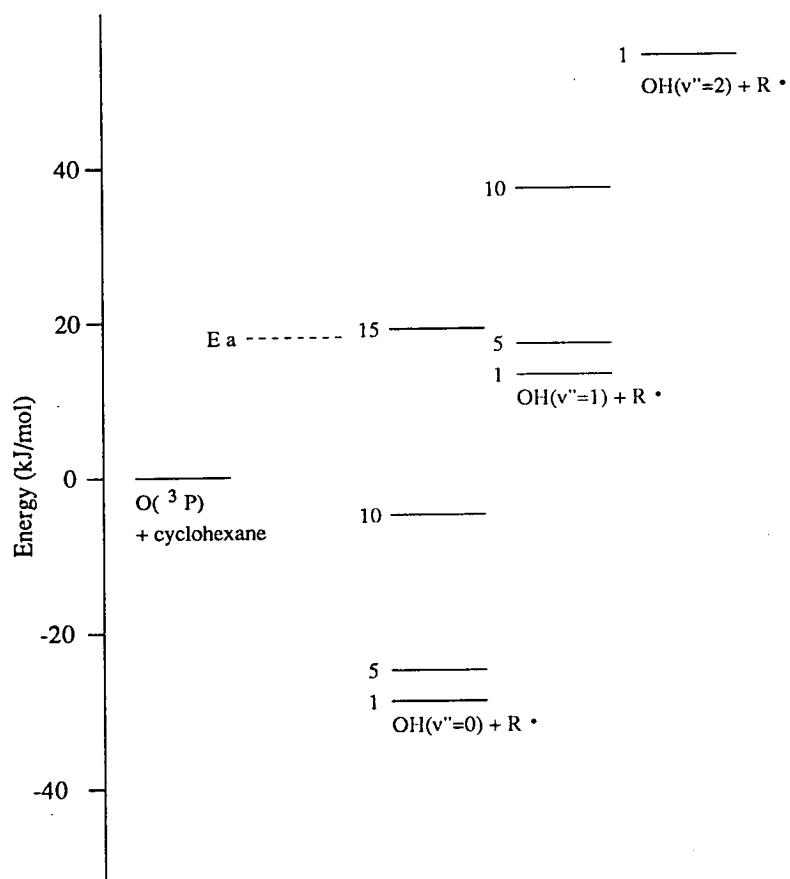


Figure 4-6: Energetics for the $O(^3P) + C_6H_{12} \rightarrow OH(X^2\Pi_{3/2}) + C_6H_{11}$ reaction system. E_a is the activation barrier and the numbering of the rotational levels, N'' , are indicated.

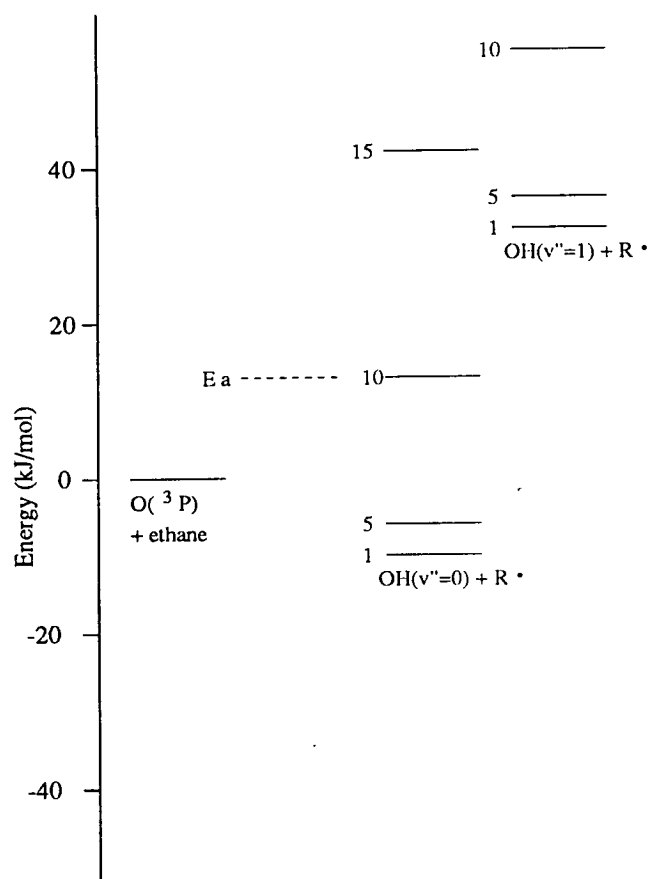


Figure 4-7: Energetics for the $\text{O}(^3\text{P}) + \text{C}_2\text{H}_6 \rightarrow \text{OH}(X^2\Pi_{3/2}) + \text{C}_2\text{H}_5$ reaction system. E_a is the activation barrier and the numbering of the rotational levels, N'' , are indicated.

337 nm Photolysis

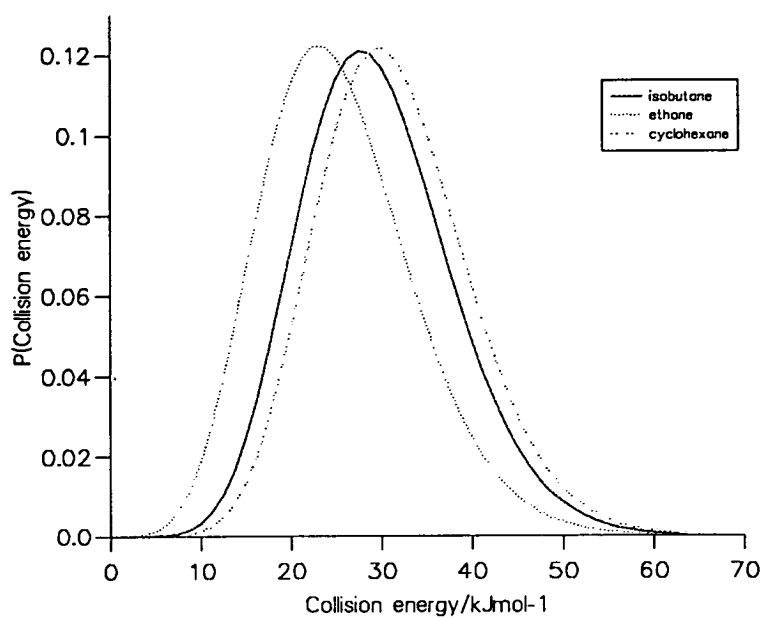


Figure 4–8: Collision energy distributions for $O(^3P) +$ hydrocarbon reactions for a photolysis wavelength of 337 nm. Only the thermal spread (equation A-7 in Appendix A) is shown.

308 nm Photolysis

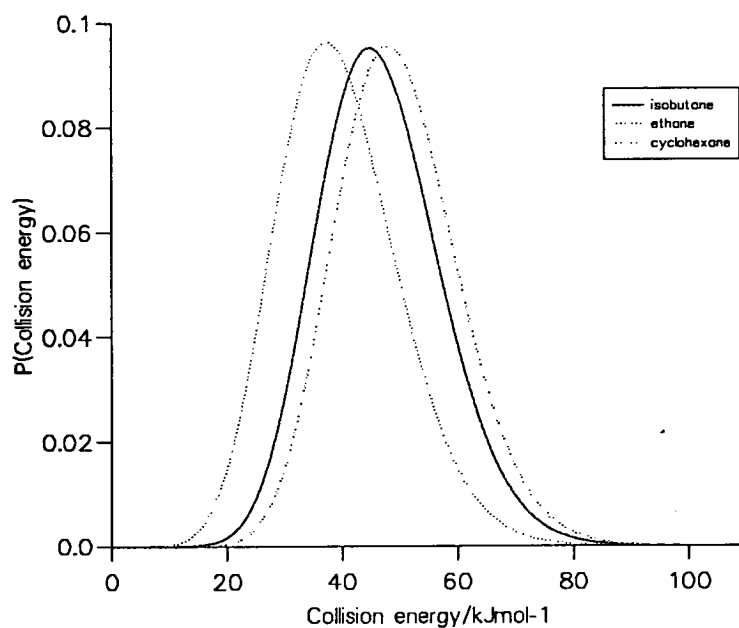


Figure 4–9: Collision energy distributions for $O(^3P) +$ hydrocarbon reactions for a photolysis wavelength of 308 nm. Only the thermal spread (equation A-7 in Appendix A) is shown.

4.2.2 Experimental

The experimental setup for a 2-laser experiment employing LIF detection was described in section 2.5.2. The reader is referred back to figure 2-13 which shows a schematic of the apparatus used for such an experiment. What follows is a brief description of the procedure pertinent to this experiment.

O(³P) atoms were generated by photolysis of NO₂ in the presence of a particular hydrocarbon using the output from the Lambda Physik EMG 100 laser operating as either a nitrogen laser (337 nm) or as a XeCl laser (308 nm). A pressure of 50-100 mTorr in the reaction chamber was maintained from the independently controlled flow of each gas and evacuation through a rotary pump. The photolysis beam was brought to a loose focus (10 × 5 mm²) at the centre of the reaction chamber. The unfocused probe beam (~3 mm radius) propagated along the same axis in the opposite direction. The probe laser was fired at an adjustable delay following the firing of the photolysis laser.

Laser-induced fluorescence was excited by tunable ultraviolet radiation in the 280-360 nm region, produced by frequency doubling the output of the Nd:YAG pumped dye laser. Fluorescence was detected in the vertical direction, perpendicular to the laser beam axis. A suitable interference filter was chosen to transmit radiation at the wavelength of the desired OH $A^2\Sigma^+ \leftarrow X^2\Pi$ vibronic transition. Signals were captured during a 1.5 μs gate (corresponding to approximately twice the OH $A^2\Sigma^+$ fluorescence lifetime), delayed by ~ 20 ns from the probe pulse to discriminate against scattered light.

4.2.3 Control and Optimisation Measurements

Several studies were performed to ensure that the observed signal was from the nascent OH product of the O(³P) + hydrocarbon reaction, and that the measured LIF line intensities gave reliable population information.

Prompt OH Background

An OH LIF signal was observed from the hydrocarbon/ NO_2 mixture in the absence of the photolysis laser. This was attributed (tentatively) to probe-laser induced photolysis of HONO i.e., the probe laser both generates and detects OH during a single laser pulse. HONO is thought to be formed by the heterogeneously catalysed reaction of $\text{H}_2\text{O} + \text{NO}_2 + \text{NO}$ [18]. To reduce the concentration of HONO the flow of NO_2 was reduced, although the flow of RH was increased to maintain the same total pressure.

Also, since the OH signal generated via HONO photolysis has a squared probe laser power dependence and the OH formed via bimolecular reaction has only a linear probe laser power dependence, then decreasing the probe power should discriminate further between the two sources of OH signal.

Both of the above measures greatly reduced the amount of OH signal observed from the probe induced photolysis of HONO. To completely remove any trace of OH signal arising from the probe induced photolysis of HONO, the multi-time delay setting facility (incorporated into the control software) was used to record a spectrum at negative Δt times (i.e. the probe laser firing before the photolysis laser) so that the probe-induced OH signal could be subtracted from the OH signal produced via bimolecular chemical reaction. This correction process is illustrated in figure 4-10. The upper panel shows a portion of the LIF excitation spectrum of the OH A-X (1,0) band from the reaction of $\text{O}(^3\text{P}) + \text{isobutane}$, with a Δt of 200 ns. Fluorescence was observed on the (1,1) band. This spectrum has contributions from both probe-laser photolysis and the products of bimolecular reactions of $\text{O}(^3\text{P})$ generated by 337 nm photolysis of NO_2 . The bottom panel of figure 4-10 shows the result of subtracting the probe induced signal ($\Delta t = -4 \mu\text{s}$) from the upper panel spectrum, leaving the contribution from bimolecular products only. It is clear that virtually all of the OH in the highest rotational states results from probe-induced photolysis. Henceforth, all spectra presented have had the background probe induced signal subtracted, unless stated otherwise.

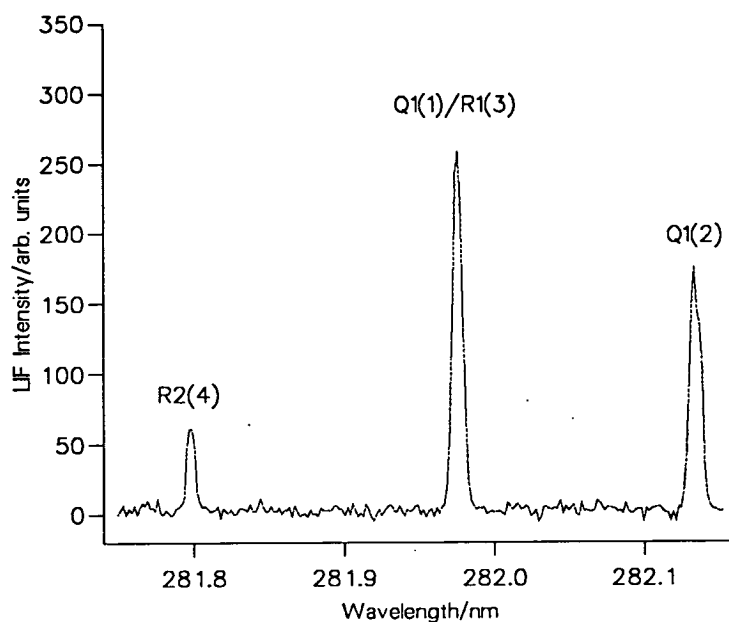
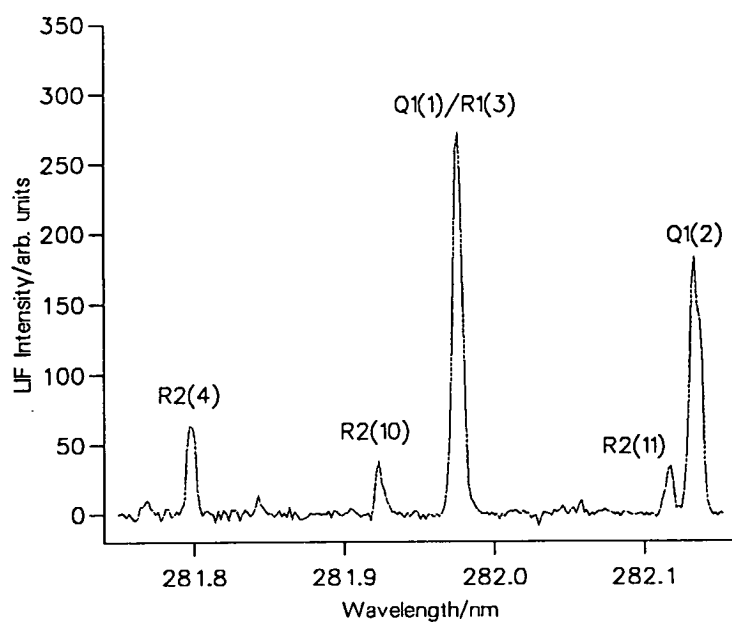


Figure 4-10: The upper panel shows the LIF excitation spectrum of the OH A-X (1,0) band from the reaction of $O(^3P) + \text{isobutane}$, with a Δt of 200 ns. Fluorescence was observed on the (1,1) band. The total pressure was 100 mTorr. The lower panel spectrum has had the probe induced signal (recorded at $\Delta t = -4\mu\text{s}$) subtracted.

Time Delay Study

The time delay between the photolysis and probe laser pulses must be sufficiently long that an observable concentration of OH product is formed, but short enough to avoid product flyout and collisional relaxation of the reactants and products. Careful preliminary measurements established a regime in which the product of the pressure, P , in the reaction chamber and the time interval, Δt , between the photolysis and probe laser pulses would be sufficiently low to ensure the observation of collisionally unmodified OH product-state distributions. Product rotational quantum-state distributions were recorded over a broad range of $P\Delta t$ values. This procedure was repeated for each hydrocarbon reactant to check for genuinely nascent OH. Measured distributions were essentially invariant for $P\Delta t$ less than 5×10^{-8} Torr s, which corresponds to ~ 0.25 gas collisions.

Saturation Effects

The OH A-X diagonal transitions ($\Delta v = 0$ progression) may easily be radiatively saturated with the probe pulse energies available from the laser system used in these experiments. A study of the effects of radiative saturation was performed prior to extracting populations from measured line intensities. Measurements were made of the ratios of main branch to satellite line intensities, where the same lower state is probed with substantially different transition probabilities. Comparison with the calculated relative transition probabilities ensured that we worked in a regime where spectra recorded were not saturated.

In the preliminary experiments of chapter 3 on the LIF of OH, a pair of Glan-Taylor prisms was used to vary the probe laser pulse energy whilst maintaining its fixed linear polarisation axis. This was achieved by adjusting the first Glan-Taylor prism with the second Glan-Taylor prism fixed to transmit only the original polarisation. In this experiment, instead of using the first Glan-Taylor prism to attenuate the transmittance of the probe laser, a Hinds PEM-80 photoelastic modulator (PEM) was used. As will be explained, this allowed several spectra, each with different probe pulse energy, to be recorded simultaneously under the same experimental conditions.

The PEM is based on a fused silica optical element, transparent at the wavelength region of interest, which vibrates at its lowest frequency of standing compression sound waves. At the centre of the element a time varying birefringence is created with a frequency equal to the natural standing sound wave frequency of the optical element itself. To sustain these vibrations the element is bonded to a quartz transducer tuned to the same frequency. In this way the amplitude of the vibrations and therefore the magnitude of the birefringence can be controlled.

The principles of operation of the PEM are illustrated in figure 4-11, which shows that the input beam can be resolved into two components, with electric vectors lying along each of the major optical axes of the optical element. When the element is compressed or elongated along one of its axes the component of the input beam lying along that axis sees an apparent change in refractive index of the element. Thus, this component of the input beam will experience a phase change (or retardance) relative to the other component on leaving the optical element, which results in a net change in the polarisation of the incident beam. The PEM optical element had a fixed oscillatory period of $20\mu\text{s}$. This meant that when the PEM was used the triggering for the experiment had to be altered. Instead of the trigger which initiates the whole of the experimental cycle coming from the PC, as described in section 2.6.1, a phase-locked output from the PEM was used to trigger all other electronics and hence maintain experimental synchronisation.

Figure 4-12 shows a schematic of the apparatus used to set up the PEM. The polarisation of the beam was modulated over a $20\mu\text{s}$ cycle by the PEM. The Glan-Taylor prism positioned after the PEM was set to transmit only the original polarisation, which means that as the polarisation of the beam emerging from the PEM changes, the amount of light of the original polarisation transmitted is modulated. This energy modulation was monitored by taking a reflection of the beam after the Glan-Taylor prism from an angled optic into a Molectron power meter (J3-090W). The Molectron power meter was connected to the transient digitiser (which was in turn connected to the control software) so that a digitised signal of the modulation could be observed over the $20\mu\text{s}$ cycle.

In this experiment the PEM was set up for half wave retardance; i.e. the PEM was allowed to operate on a linearly polarised beam to produce, at the

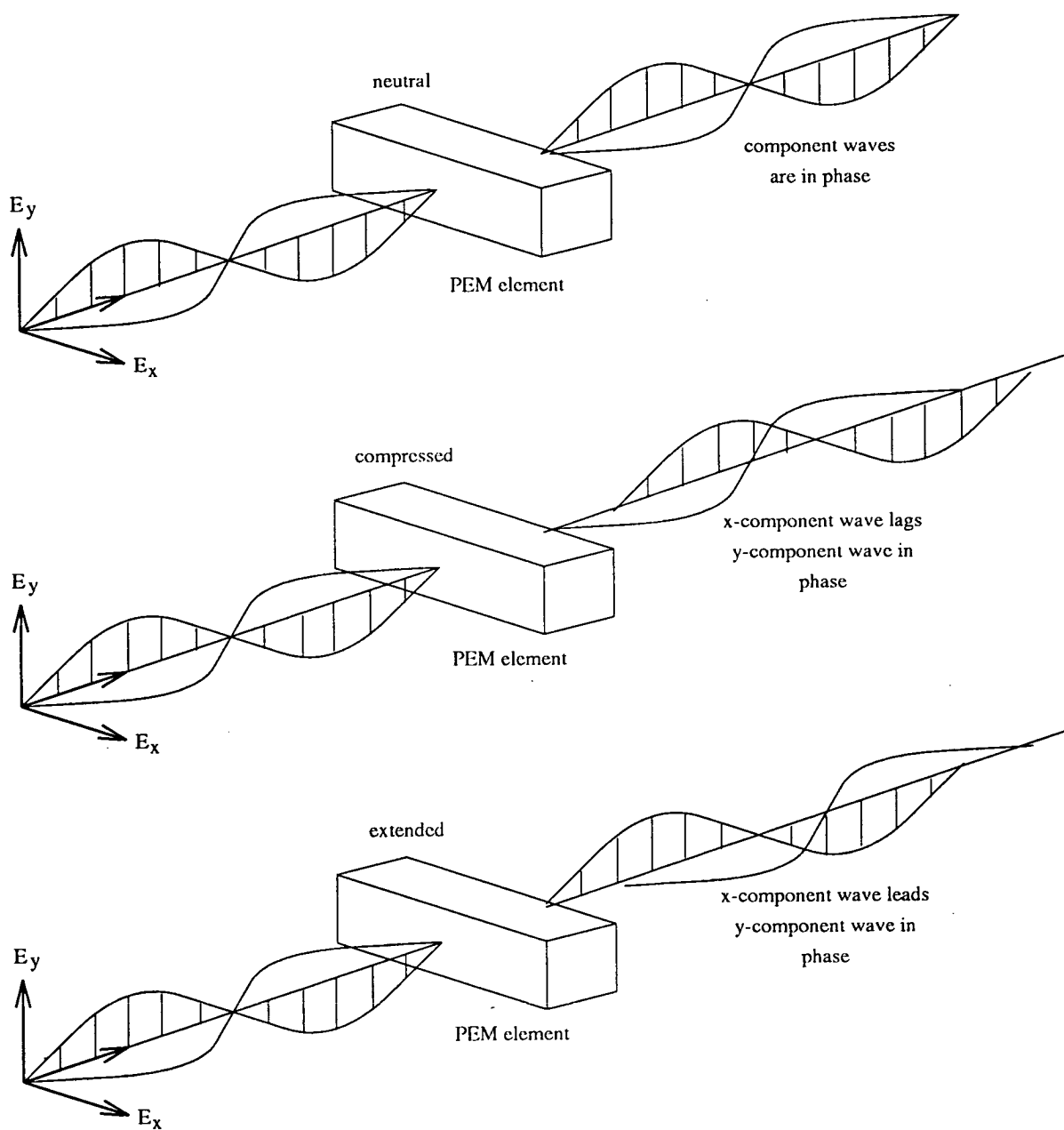


Figure 4-11: Schematic showing the principles of operation of a photoelastic modulator

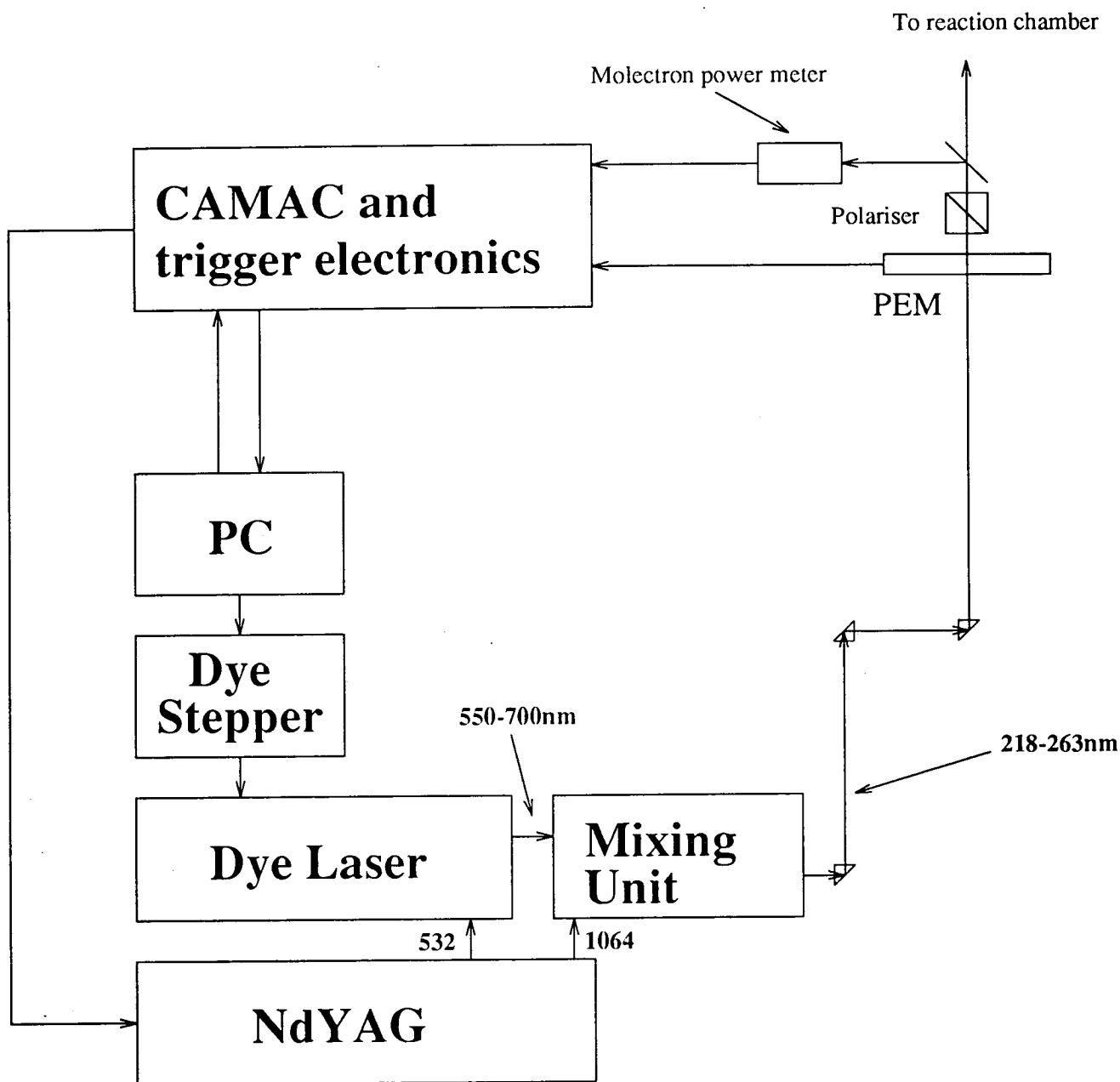


Figure 4-12: Schematic of the experimental setup used for probe laser power modulation using the Hinds PEM-80 photoelastic modulator.

maximum compression or extension, a linearly polarised beam at 90 degrees to the incident beam. The beam incident on the PEM was vertically polarised and the Glan-Taylor prism was set to transmit either only vertically or only horizontally polarised light. The resultant probe energy modulation is shown in figure 4-13 for both settings of the Glan-Taylor prism.

In conclusion, by choosing several different time delay settings for firing the probe laser within the $20\mu\text{s}$ cycle of the PEM, it was possible to record several spectra of different probe pulse energies (but fixed polarisation) simultaneously. The photolysis laser to probe laser delay was kept fixed during these measurements.

It was found that, for excitation on the stronger diagonal ($\Delta v = 0$) bands, pulse energies less than $\sim 50\ \mu\text{J}$ were sufficiently low to produce an essentially linear proportionality of the observed LIF signal on the excitation pulse energy. For the weaker off-diagonal ($\Delta v = -1$) transitions, pulse energies less than $\sim 500\ \mu\text{J}$ were adequate for linear response. This is in agreement with a previous study of such effects[19].

4.2.4 Relative Population Measurements from Intensity Measurements

OH product populations were extracted from LIF excitation spectra. Data were collected on all the major branches of the A-X transition, allowing the fine structure and Λ -doublet populations to be determined.

To reduce the observed LIF intensities to rotational populations the following procedure was used. First of all the concentration of molecules, $U(J')$, excited to the $A^2\Sigma^+$ electronic state from the $X^2\Pi$ ground electronic state could be estimated by dividing the intensity of the measured fluorescence signal, resulting from the initial excitation, by the sensitivity with which the fluorescence was detected, i.e.

$$U(J') = \frac{I(J')}{D(J')} \quad (4.2)$$

$I(J')$ is the measured integrated LIF intensity resulting from the initial laser excitation to the upper J' rotational level. $D(J')$ is a detection sensitivity which can

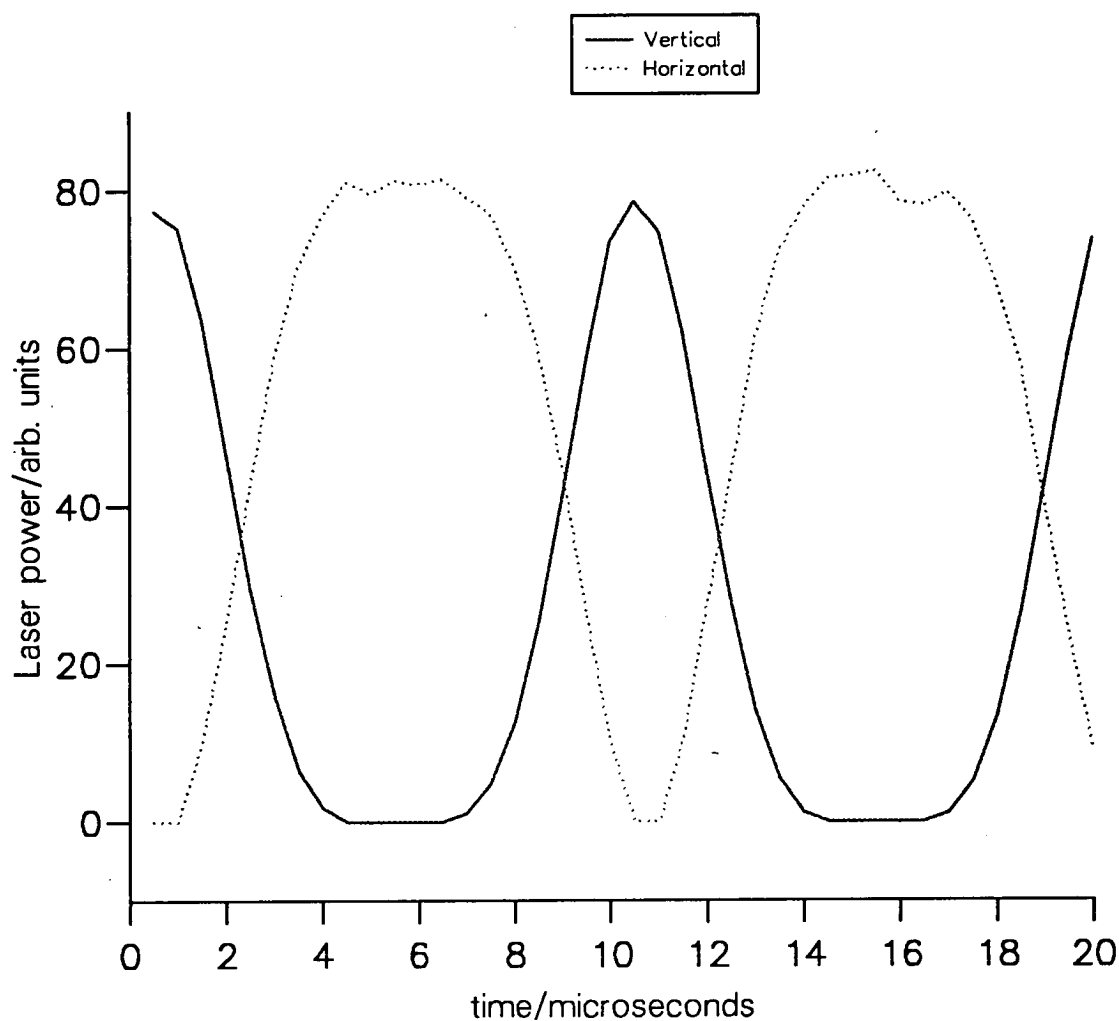


Figure 4-13: Probe laser power modulation using the photoelastic modulator, where the solid line indicates Glan-Taylor transmittance of vertically polarised light only and the dashed line indicates transmittance of horizontally polarised light only. The time axis corresponds to the delay between the start of the phased reference output pulse from the PEM and the optical pulse passing through the PEM element.

be written as

$$D(J') = \sum_6 F(J', J'') T(\lambda) P(J', J'') \quad (4.3)$$

The six beneath the summation refers to the sum over the six possible branches in fluorescence after the initial excitation. $T(\lambda)$ is the product of the wavelength-dependent transmission for the interference filter and the photomultiplier tube for a particular emitting transition. The transmission of the filter and the detection sensitivity of the PMT were taken from manufacturer's specifications. $P(J', J'')$ is a function which allows for the small polarisation corrections required when exciting LIF with a linearly polarised laser[20]. Finally $F(J', J'')$ refers to the fraction of fluorescence carried by each emitting line and can be expressed as

$$F(J', J'') = \frac{S(J', J'') \nu^4}{\sum_6 S(J', J'') \nu^4} \quad (4.4)$$

$S(J', J'')$ is the rotational linestrength factor, values of which have been calculated from the formulae recommended by Dieke and Crosswhite[21]. Each $S(J', J'')$ is weighted by ν^4 for the particular line to account for the fact that the rate of emission is proportional to ν^3 through the Einstein A factor, and further that we detect the energy of the photons rather than count the photons themselves. This procedure implicitly assumes that the fluorescence lifetime does not vary significantly over the range of J' sampled[28].

The lower state rotational populations, $L(J'')$, were then obtained by dividing the upper state population by the linestrength of the exciting transition, which itself is divided by its own degeneracy i.e.,

$$L(J'') = \frac{U(J')}{[S(J', J'')_{excit} / (2J'' + 1)]} \quad (4.5)$$

For overlapping lines (usually the main line and it's associated satellite) the fraction of the measured fluorescence intensity from the main line only could be evaluated from the known linestrengths and detection sensitivities. For example, for the $R_1(1)$ line and its satellite $R_{21}(1)$, the fraction of the observed total integrated area of the LIF signal on the overlapped lines due to the $R_1(1)$ line is

$$\frac{S[R_1(1)] D[R_1(1)]}{S[R_1(1)] D[R_1(1)] + S[R_{21}(1)] D[R_{21}(1)]} \quad (4.6)$$

4.2.5 Measured OH State Distributions: Results and Discussion

We have measured the nascent population distributions of the OH product from the reactions of $O(^3P) + RH \rightarrow OH + R\cdot$ for primary (RH =ethane), secondary (RH =cyclohexane) and tertiary (RH = isobutane) hydrogen abstraction. Each reaction was studied at two average collision energies corresponding to 337 nm and 308 nm photolysis of NO_2 .

Rotational Distributions

Reference back to table 4-1 (which lists the mean collision energies for the above reactions) and figures 4-5 to 4-7 (which illustrate the reaction energetics) shows that the reaction of $O(^3P) +$ isobutane at a photolysis wavelength of 337 nm is capable of populating the $OH(v''=0)$ level up to $J''\sim 17$ and the $OH(v''=1)$ level up to $J''\sim 12$. The situation is similar for cyclohexane. For ethane only rotational levels up to $J''\sim 12$ in the ground vibrational level of OH can be populated, with $OH(v''=1)$ being energetically inaccessible for all but the high energy tail of the $O(^3P)$ distribution.

Figures 4-14 and 4-15 show LIF excitation spectra of the $R_1(N'')$ branches probing the rotational levels of the ground and first vibrational levels of the OH product from the $O(^3P) +$ isobutane reaction. Similar spectra probing rotational levels of the ground vibrational levels of the OH product from the $O(^3P) +$ cyclohexane and $O(^3P) +$ ethane reactions are shown in figures 4-16 and 4-17, respectively. The rotational populations resulting from the measured intensities representing the average of 4 repeated measurements, for each of the reactions, are shown in figures 4-18 and 4-19. These show that for both $OH(v''=0)$ and $OH(v''=1)$, and for all the hydrocarbons, there is a general monotonic decrease in the rotational populations from $N''=1$. Rotational levels up to $N''=9$ are populated to a measurable extent in $OH(v''=0)$ for all the reactions, although the reduced signal to noise for the $O(^3P)$ ethane reaction makes it more difficult to extract accurate populations for the higher less intense rotational levels. Populations up to only $N''=6$ are apparent in figure 4-19 for the $OH(v''=1)$ product for the $O(^3P) +$ isobutane

reaction and the distribution declines with N'' significantly more rapidly than for $\text{OH}(v''=0)$. Although no distribution was recorded for the $\text{O}(^3\text{P}) + \text{cyclohexane} \rightarrow \text{OH}(v''=1) + \text{C}_6\text{H}_{11}$ reaction, $\text{OH}(v''=1)$ was easily detected from this reaction. There was *no* detectable $\text{OH}(v''=1)$ from the reaction $\text{O}(^3\text{P}) + \text{ethane}$, in agreement with the anticipated reaction energetics.

Very similar distributions were obtained at an NO_2 photolysis wavelength of 308 nm. Figures 4-20 and 4-21 show $R_1(N'')$ branch spectra of the $\text{OH}(v''=0)$ and $\text{OH}(v''=1)$ products for each of the $\text{O}(^3\text{P}) + \text{hydrocarbon}$ reactions. The corresponding rotational distributions are shown in figures 4-22 and 4-23. It is interesting to note that the previously energetically "forbidden" reaction of $\text{O}(^3\text{P}) + \text{ethane}$ at a photolysis wavelength of 337 nm becomes accessible at 308 nm, again in agreement with the expected reaction energetics.

The obvious general conclusion to be reached from the rotational distributions for $\text{O}(^3\text{P}) + \text{hydrocarbon}$ reactions is that the OH product is formed with very little rotational excitation even though the energetics permit much higher rotational levels to be populated. Figures 4-24 and 4-25 summarise the rotational distributions obtained for $\text{OH}(v''=0)$ and $\text{OH}(v''=1)$ for the $\text{O}(^3\text{P}) + \text{isobutane}$ reaction, for both 337 nm and 308 nm photolysis wavelengths. It is evident from these plots that the collision energy does not have any dramatic effects on the rotational distributions. These plots can be directly compared with figure 4-26 which shows the results achieved by Luntz *et al* [2] using the crossed molecular beam method. Our results are shown to be consistent with those of Luntz *et al*. The results obtained for the rotational distributions in our experiments were summarised by calculating the fraction of available energy appearing in rotation, f_{rot} , of the OH product, for each of the $\text{O}(^3\text{P}) + \text{hydrocarbon}$ reactions, at each of the NO_2 photolysis wavelengths. This fraction can be written as

$$f_{\text{rot}} = \frac{\langle E_{\text{rot}} \rangle}{\langle E_{\text{avail}} \rangle} \quad (4.7)$$

where

$$\langle E_{\text{avail}} \rangle = \Delta H_0 + E_{\text{colln}} \quad (4.8)$$

ΔH_0 is the reaction exothermicity and E_{colln} is the average collision energy. $\langle E_{\text{rot}} \rangle$ is the average energy in rotation for a particular vibrational level and can be

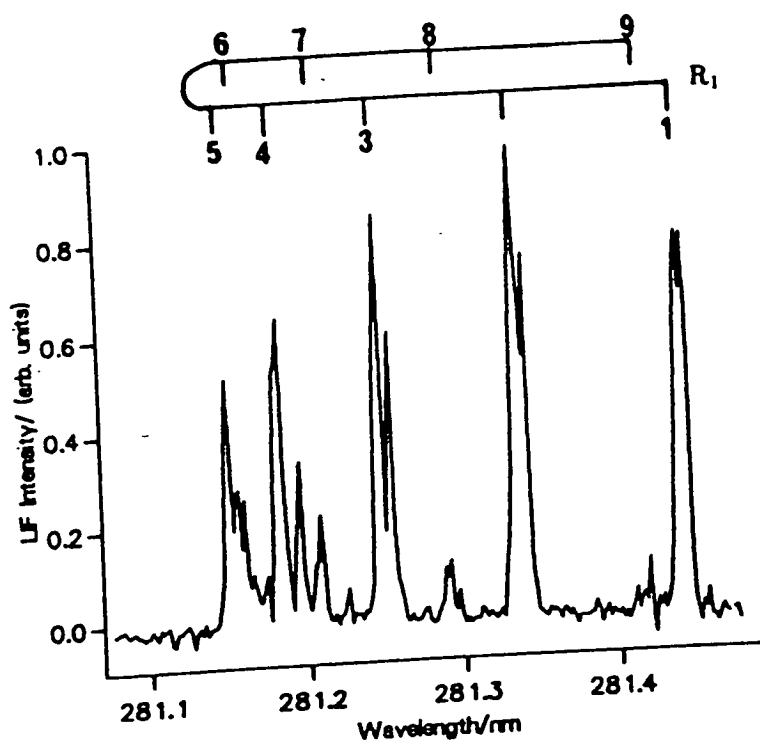


Figure 4-14: LIF excitation spectrum of the R₁ branch region of the OH A-X (1,0) band from the reaction O(³P) + isobutane at a photolysis wavelength of 337 nm. Fluorescence was observed on the (1,1) band. Experimental conditions: total pressure, 100 mTorr; $\Delta t=200$ ns; probe power, 150 μ J.

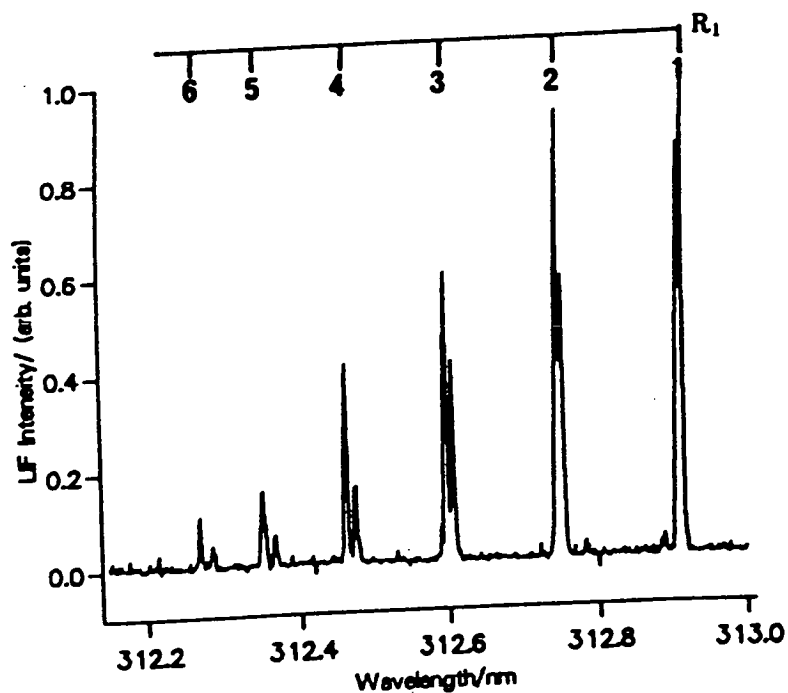


Figure 4-15: LIF excitation spectrum of the R₁ branch region of the OH A-X (1,1) band from the reaction O(³P) + isobutane at a photolysis wavelength of 337 nm. Fluorescence was observed on the (1,0) band.

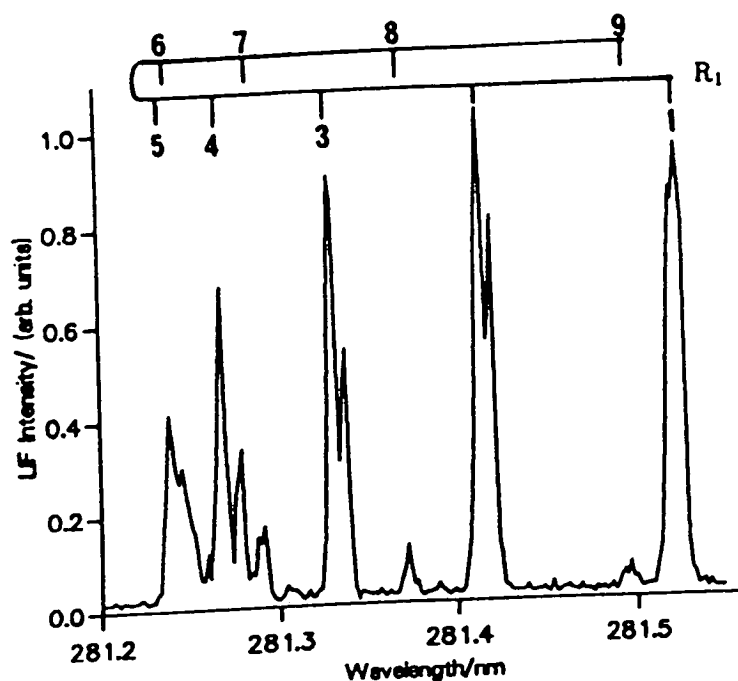


Figure 4-16: LIF excitation spectrum of the R₁ branch region of the OH A-X (1,0) band from the reaction $O(^3P) + \text{cyclohexane}$ at a photolysis wavelength of 337 nm. Fluorescence was observed on the (1,1) band. Experimental conditions: total pressure, 100 mTorr; $\Delta t = 200$ ns; probe power, 200 μJ .

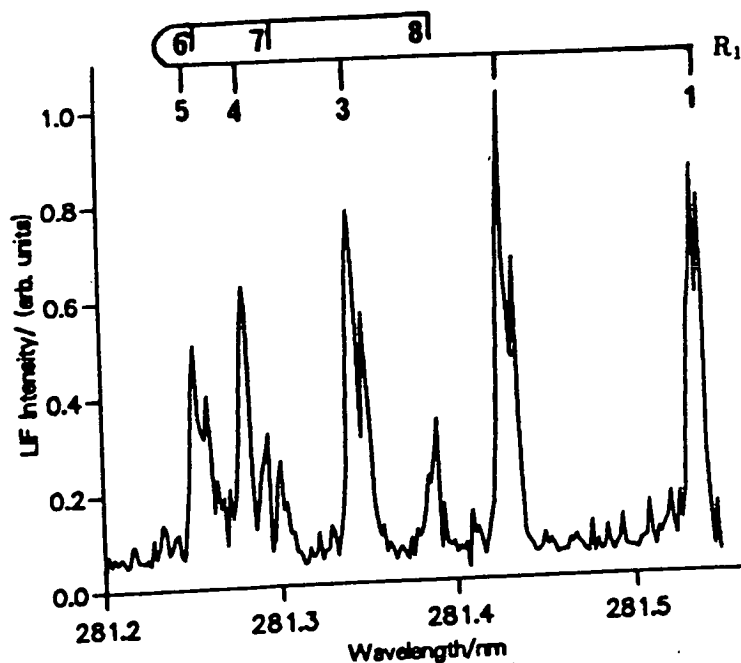


Figure 4-17: LIF excitation spectrum of the R₁ branch region of the OH A-X (1,0) band from the reaction $O(^3P) + \text{ethane}$ at a photolysis wavelength of 337 nm. Fluorescence was observed on the (1,1) band.

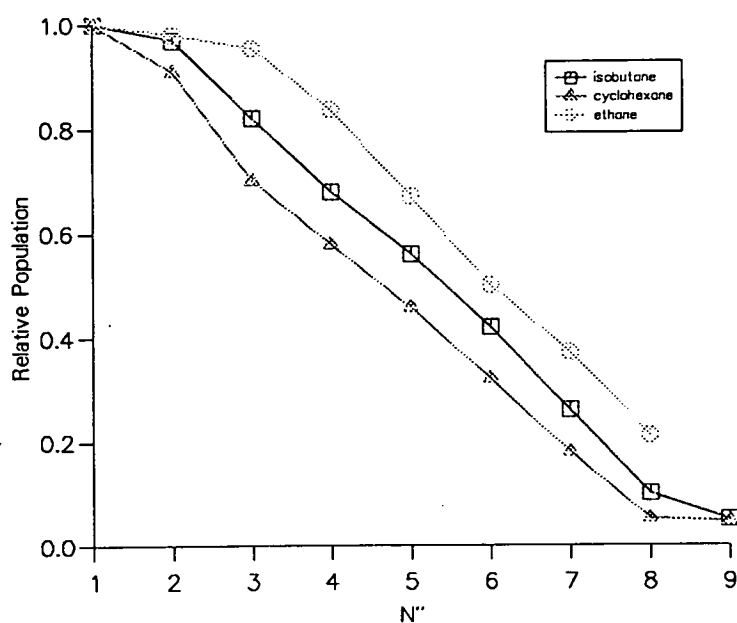


Figure 4-18: Relative rotational state populations of the $\text{OH}(v''=0)$ product in the $^2\Pi_{3/2}$ fine structure component produced in the reaction $\text{O}(^3\text{P}) + \text{RH}$ at a photolysis wavelength of 337 nm. The populations were determined from the repeated measurements of LIF excitation spectra of the type shown in figure 4-14 for isobutane, figure 4-16 for cyclohexane and figure 4-17 for ethane.

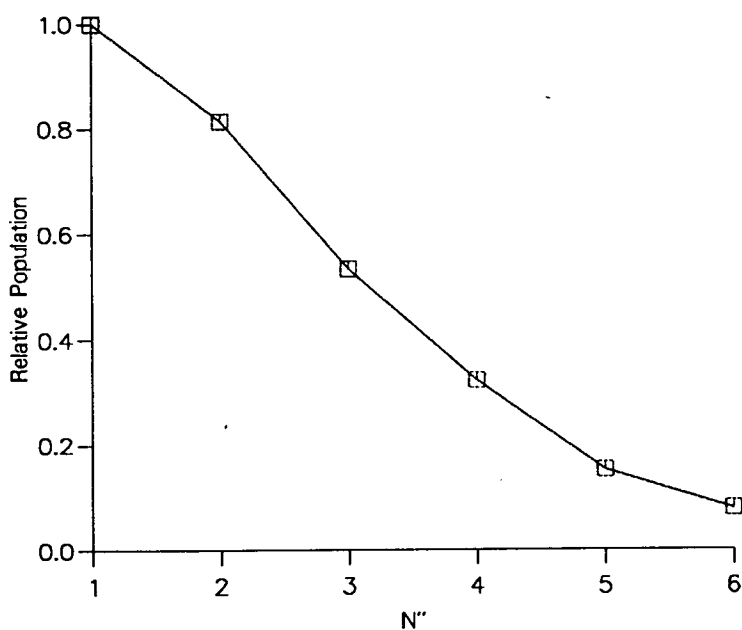


Figure 4-19: Relative rotational state populations of the $\text{OH}(v''=1)$ product in the $^2\Pi_{3/2}$ fine structure component produced in the reaction $\text{O}(^3\text{P}) + \text{isobutane}$ at 337 nm. The populations were determined from the repeated measurements of LIF excitation spectra of the type shown in figure 4-15.

$f_{rot}, 337 \text{ nm}, v''=0$	$f_{rot}, 337 \text{ nm}, v''=1$	$f_{rot}, 308 \text{ nm}, v''=0$	$f_{rot}, 337 \text{ nm}, v''=1$
0.05	0.03	0.04	0.02
0.06	-	0.05	0.02
0.12	0.00	0.08	0.03

Table 4-2: Fraction of available energy appearing in rotation for each of the $O(^3P) + RH$ reactions (isobutane first row, cyclohexane second row and ethane last row), for the $v''=0$ and $v''=1$ vibrational levels, at each of the NO_2 photolysis wavelengths. The blank entry signifies that no measurement was made. The values quoted represent the average of 5 measurements and each one had a spread of $\sim 5\%$.

written as

$$\langle E_{rot} \rangle = \sum_{N''} P(N'') E_{rot}(N'') \quad (4.9)$$

$P(N'')$ is the fractional population in each rotational level, N'' (normalised to unity over all N''), and E_{rot} is the rotational energy of the particular level. The results are shown in table 4-2. From this table it can be seen that very little of the available reaction energy appears in rotational excitation of the OH product. The fraction of rotational excitation in the $OH(v''=0)$ product is shown to be approximately twice that of $OH(v''=1)$. Although Luntz *et al* stated that rotational excitation accounts for only 2% of the total reaction energy, they did not tabulate specific rotational partitioning for each of the different $O(^3P) + RH$ reactions as we have done. It is interesting to note there is a higher fraction of energy in rotation for the $O(^3P) + \text{ethane}$ reaction. This does not correlate with reaction exothermicity and must therefore be controlled by dynamic rather than energetic effects. We speculate that there is an increase in the cone of acceptance for this reaction compared to secondary and tertiary H-abstraction reactions.

The effect of varying the collision energy is also shown in this table since each reaction was studied at two NO_2 photolysis wavelengths. The large spreads in each of the collision energies (due to the thermal motions of the reagents and precursor molecules, and the distribution of internal states in the NO co-fragment) meant that only a very crude variation of the collision was possible. However, it is clear that there is extra collision energy available at an NO_2 photolysis wave-

length of 308 nm since the $\text{OH}(v''=1)$ product channel opens up for the $\text{O}(^3\text{P}) + \text{ethane}$ reaction. In general, table 4-2 indicates that the collision energy has a very minor effect on the degree of rotational excitation of the OH product. This is in agreement with the “propensity rules”[29] (which attempt to predict those product states that will be most populated from a reaction) for the $\text{H} + \text{LH}'$ mass combination and predict that the extra translational energy in the reagents is predominantly converted into extra translational energy of the products. These rules also predict significant internal excitation of the HL product and indeed this has been found to be true for certain cases, examples include $\text{O}(^3\text{P}) + \text{HBr} \rightarrow \text{OH} + \text{Br}$ [19] where about 75% of the available energy is converted into internal excitation of the OH product and $\text{F} + \text{HBr} \rightarrow \text{HF} + \text{Br}$ [30] where about 70% of the available energy is converted into internal excitation of the HF product. The $\text{H} + \text{LH}'$ mass combination actually results in inefficient conversion of reagent orbital angular momentum into product diatomic rotational angular momentum and rotation in the HL product is attributed to a repulsive interaction in breaking the L-H' bond. Because the centre-of-mass of the HL product lies very close to the heavy particle, forces acting on the light end of the molecule, through bent geometries, impart a large torque and convert the repulsive energy into product rotation[32]. It is clear from both our results and those of Luntz[2] that the very cold rotational distributions obtained for the $\text{O}(^3\text{P}) + \text{hydrocarbon}$ reactions contradict the general propensities for the $\text{H} + \text{LH}'$ kinematic category. Based on discussions of rotational excitation from previous work[22] for $\text{O}(^3\text{P}) + \text{hydrocarbon}$ reactions, Luntz *et al*[2] attributed the cold rotational distributions to a collinear approach of the $\text{O}(^3\text{P})$ atom to the particular C-H bond. These predictions were supported by QCT calculations on model potential energy surfaces[31] which gave relatively good global predictions of the dynamics of all classes of $\text{O}(^3\text{P}) + \text{RH}$ reaction (primary, secondary and tertiary). A much more revealing aspect in describing the dynamics of $\text{O}(^3\text{P}) + \text{hydrocarbon}$ reactions has been carried out by McKendrick *et al*[19] by considering the *angular* dependence of the potential energy surfaces. These should relate more closely to the rotational distributions measured since O-H-R bending motions correlate asymptotically with OH product rotation. Calculations were performed that showed that the barrier to reaction increased rapidly with O-H-R bending angle. The rapid increase of the reaction barrier height for

$O(^3P) + RH$ reactions restricts the range of energetically accessible transition-state geometries, therefore reactions are channeled through configurations with a narrow distribution about the collinear minimum-energy path. These results confirmed the more speculative ones of Luntz[31]. The above discussion leads us to predict that (a) the angular scattering of the OH product should be *backward*, and (b) the reaction cross-section should *decline* with rotation of the RH reagent. Addressing point (a), it is interesting to note that recent work by Zare *et al*[33] on a superficially similar system, $Cl + CH_4(v'') \rightarrow HCl + CH_3$, which also produces rotationally cold product of abstraction of an H atom from a hydrocarbon suggests that the angular scattering is predominantly *forward*. This is surprising, and suggests that a future experiment aimed at measuring the OH *angular* scattering for $O(^3P) +$ hydrocarbon reactions could be very revealing. On point (b), an excellent future experiment would be to promote the $O(^3P) + CH_4$ reaction by selective excitation of the CH_4 into chosen rovibrational states. This reaction is particularly attractive because there is no interference from the reaction of $O(^3P)$ with ground state methane since it is energetically unreactive.

Spin-orbit propensities

Spin-orbit ratios were measured for the $OH(v''=0)$ product from the $O(^3P) +$ isobutane reaction at both photolysis wavelengths of 337 nm and 308 nm. Measurements were made using the ratio of $P_1(N'')/P_2(N'')$ since the P lines are the least overlapped. It can be seen from figure 4-27 that there is a reproducible preference for population of the lower, $^2\Pi_{3/2}$, spin-orbit state. Included in the figure are the results obtained by Luntz *et al*[2] which are seen to be consistent with ours. Luntz *et al* attempted to explain the preference in spin-orbit states by comparing the different possible potential energy surfaces that reaction could take place upon. Figure 4-28 is a schematic correlation diagram showing the possible reactive surfaces (where the correlations are drawn from the fact that the vector sum of spin and orbital momentum, the total angular momentum, must be conserved in the adiabatic limit). $O(^3P_2)$ correlates with $OH(^2\Pi_{3/2})$ through a $^3\Pi_2$ surface; $O(^3P_0)$ correlates with $OH(^2\Pi_{1/2})$ through a $^3\Pi_0$ surface; while $O(^3P_1)$ does not correlate with $OH(^2\Pi)$ at all but rather with a nonreactive $^3\Sigma$ surface.

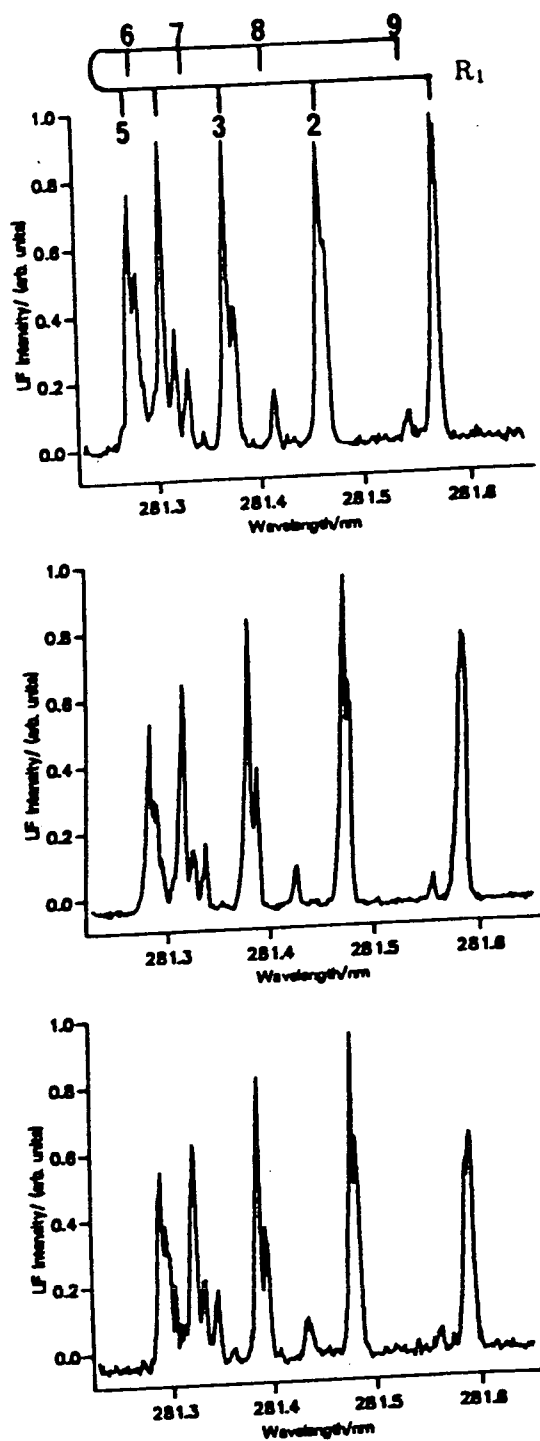


Figure 4-20: LIF excitation spectra of the OH A-X (1,0) band from the reactions $O(^3P)$ + isobutane (top panel), $O(^3P)$ + cyclohexane (centre panel) and $O(^3P)$ + ethane (bottom panel), all at a photolysis wavelength of 308 nm. Fluorescence is observed on the (1,0) band. Experimental conditions were the same for each of the spectra namely: total pressure 100 mTorr, $\Delta t=200$ ns, probe power, 100 μJ .

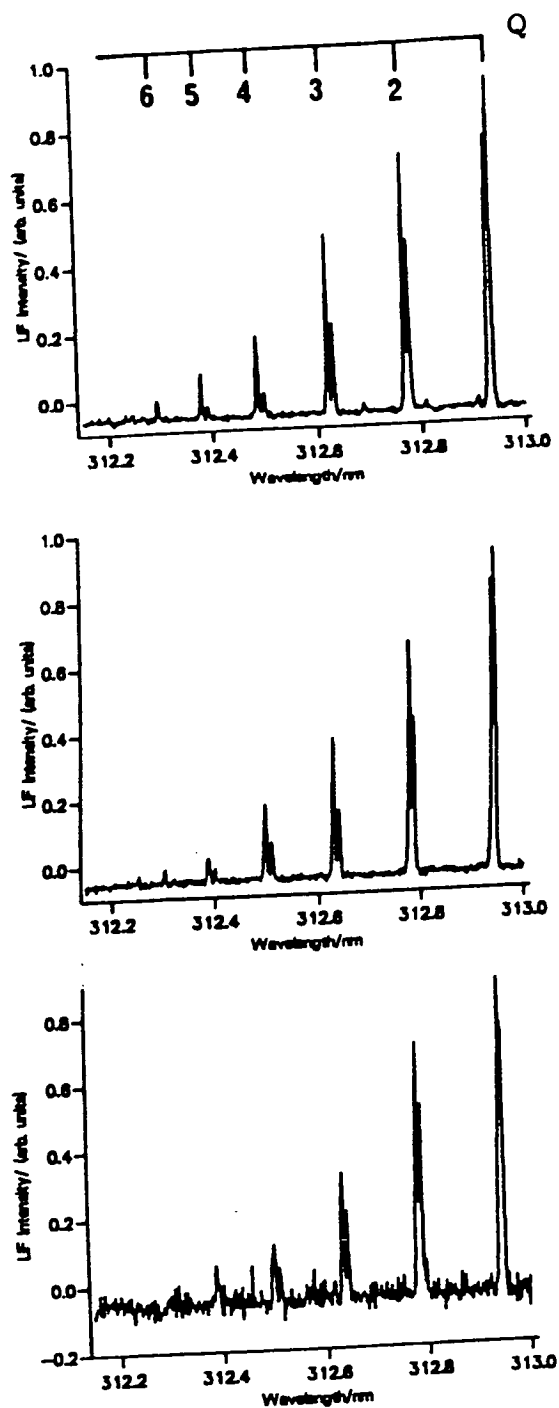


Figure 4-21: LIF excitation spectra of the OH A-X (2,1) band from the reactions $O(^3P)$ + isobutane (top panel), $O(^3P)$ + cyclohexane (centre panel) and $O(^3P)$ + ethane (bottom panel), all at a photolysis wavelength of 308 nm. Fluorescence is observed on the (2,1) band. Experimental conditions were the same for each of the spectra namely: total pressure 100 mTorr, $\Delta t=200$ ns, probe power, 100 μ J.

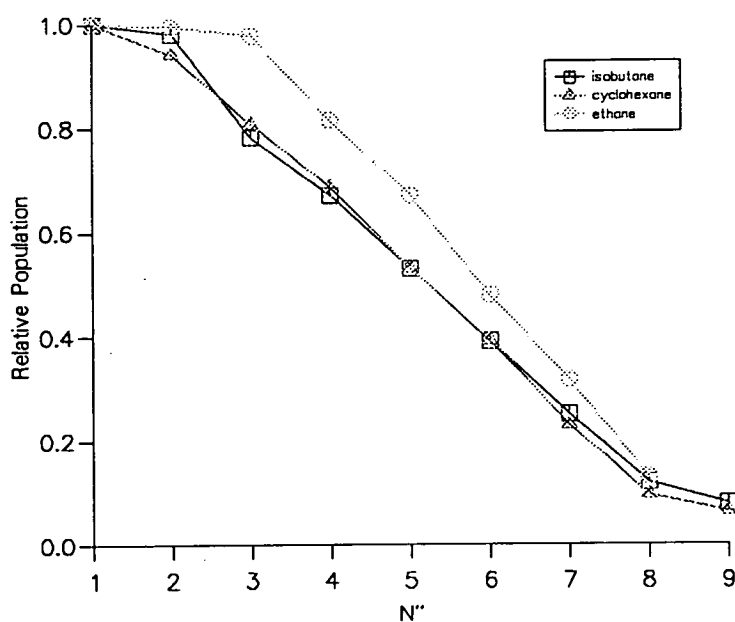


Figure 4-22: Relative rotational state populations of the OH($v''=0$) product in the $^2\Pi_{3/2}$ fine structure component produced in the reaction $O(^3P) + RH$ at 308 nm. The populations were determined from the intensities shown in figure 4-18.

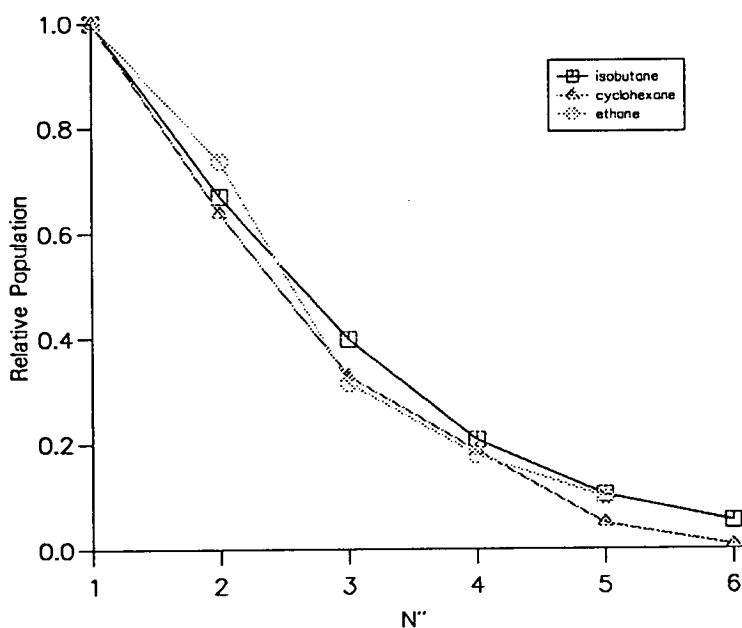


Figure 4-23: Relative rotational state populations of the OH($v''=1$) product in the $^2\Pi_{3/2}$ fine structure component produced in the reaction $O(^3P) + RH$ at 308 nm. The populations were determined from the intensities shown in figure 4-19.

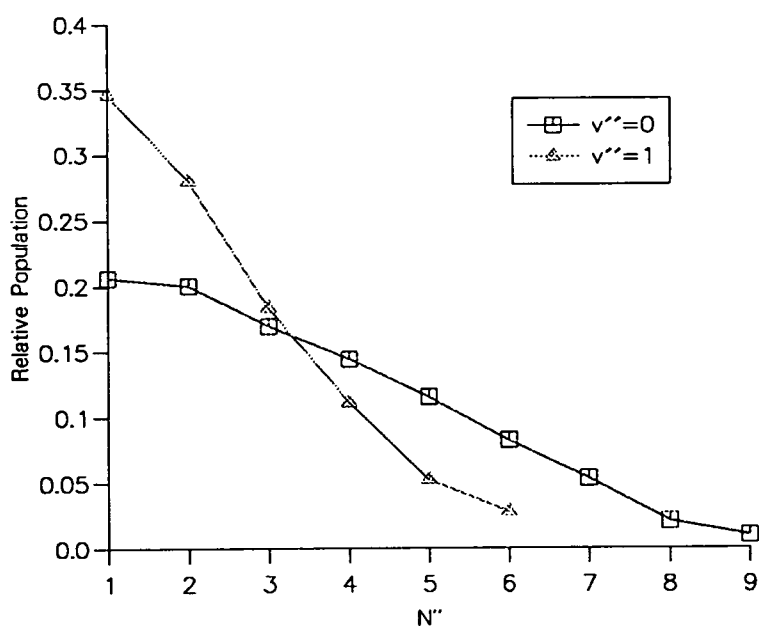


Figure 4-24: Relative rotational state populations of the OH($v''=0, 1$) products in the $^2\Pi_{3/2}$ fine structure component produced in the reaction $O(^3P) + \text{isobutane}$ at a collision energy of 29.6 kJ mol⁻¹ (337 nm photolysis). The populations are normalised so that the total scattering into each vibrational level is unity.

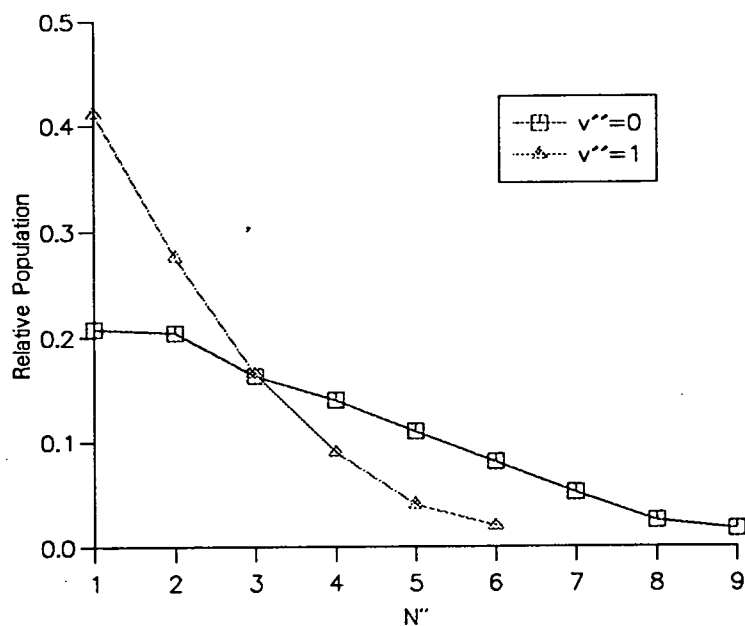


Figure 4-25: Relative rotational state populations of the OH($v''=0, 1$) products in the $^2\Pi_{3/2}$ fine structure component produced in the reaction $O(^3P) + \text{isobutane}$ at a collision energy of 46.6 kJ mol⁻¹ (308 nm photolysis). The populations are normalised so that the total scattering into each vibrational level is unity.

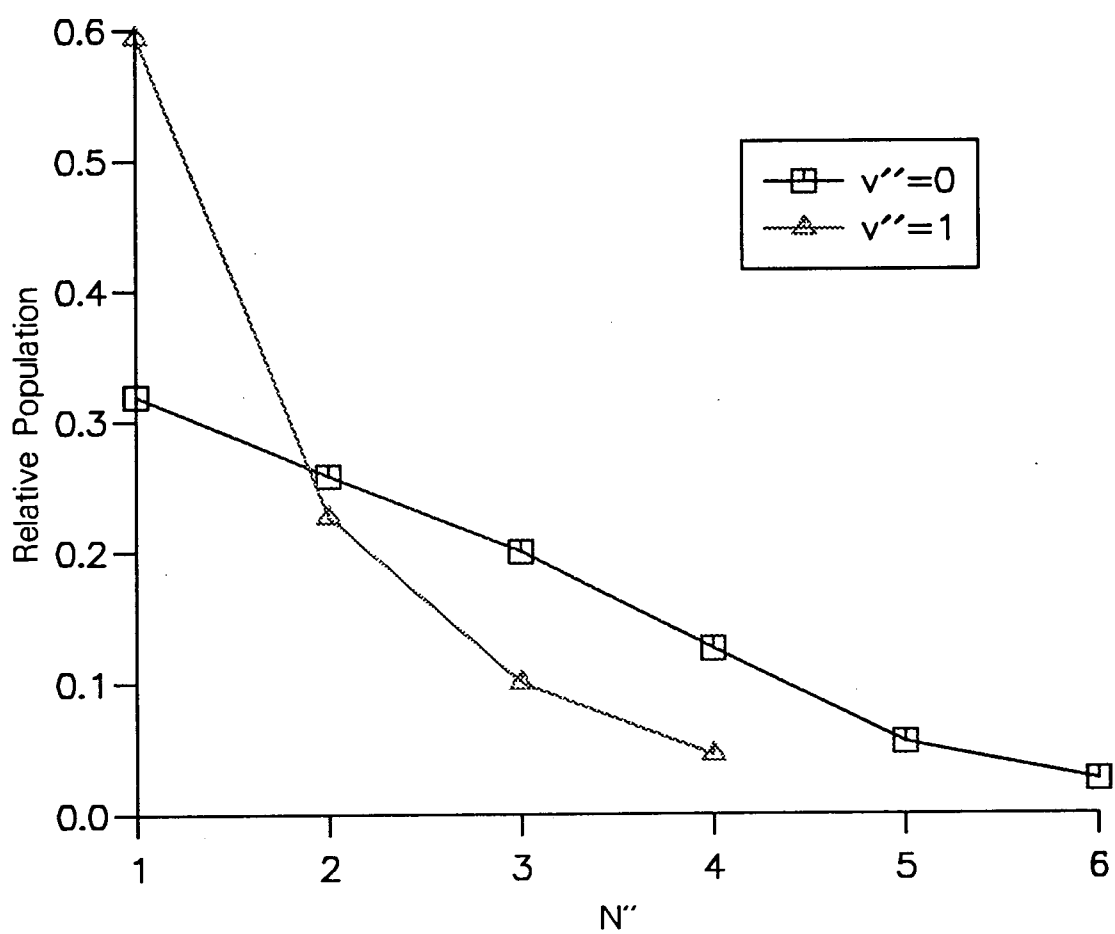


Figure 4–26: Relative rotational state populations of the $\text{OH}(v''=0, 1)$ products in the $^2\Pi_{3/2}$ fine structure component produced in the reaction $\text{O}(^3\text{P}) + \text{C}_6\text{H}_{12}$ at a collision energy of 29.7 kJ mol^{-1} , from reference [2]

Therefore in the adiabatic limit, where no collision induced transitions between surfaces can take place, the ratio of $\Pi_{3/2}$ to $\Pi_{1/2}$ products is seen to depend on the initial $O(^3P_2)$ to $O(^3P_0)$ ratio. Luntz *et al* produced $O(^3P)$ via the microwave discharge of O_2 , where the relative spin-orbit populations were estimated from EPR experiments[23] to be $\sim 72\%O(^3P_2)$, $\sim 22\%O(^3P_1)$ and $\sim 6\%O(^3P_0)$. In the adiabatic limit they could therefore expect to produce OH with the distribution $\Pi_{3/2}/\Pi_{1/2}=12$. For the photolysis of NO_2 at 337 nm the relative spin-orbit populations have been measured to be 82% $O(^3P_2)$, 16% $O(^3P_1)$ and 2% $O(^3P_0)$ (see section 4.1). No such values could be found for the 308 nm photolysis of NO_2 . However, as discussed in section 4.1 the relative spin-orbit populations have been found to be fairly invariant at NO_2 photolysis wavelengths at 337 nm and 266 nm. We have assumed that the distribution at a photolysis wavelength of 308 nm are similar to those produced at 337 nm. In the adiabatic limit therefore, a $\Pi_{3/2}$ to $\Pi_{1/2}$ ratio of ~ 40 is expected using the $O(^3P_J)$ population values produced via photolysis. In the diabatic limit, where there are many transitions between the surfaces during the course of the collision the corresponding result would be $(^2\Pi_{3/2}/^2\Pi_{1/2})=1$ for any method of generation of $O(^3P)$. From figure 4-27 it can be seen that the $\Pi_{3/2}/\Pi_{1/2}$ ratio lies between 1.5 and 1.82 for both our results and those achieved by Luntz[2]. Since the $\Pi_{3/2}$ to $\Pi_{1/2}$ ratio is essentially the same for the alternative methods of $O(^3P)$ production (which have significantly different $^3P_2$ to $^3P_0$ ratios), and because this ratio is so close to unity suggests that the reactions of $O(^3P)$ + saturated hydrocarbons lie much closer to the diabatic limit and therefore depend on what PES the reaction *exits* upon, being independent of the reaction entrance channel.

Λ -doublet Propensities

The phenomenon of Λ doubling in chemical reaction dynamics may seem to be a minute spectroscopic effect, and it is true that the corresponding energetic splitting is normally completely negligible compared to other internal energies or to collision energies. However preferential population of one member of a Λ -doublet pair has been observed in chemical reactions (for example, in the OH product of the reactions $O(^1D) + RH \rightarrow OH + R\cdot$ [24] and $^{16}O(^1D) + H_2^{18}O \rightarrow O^{16}H + O^{18}H$ [25])

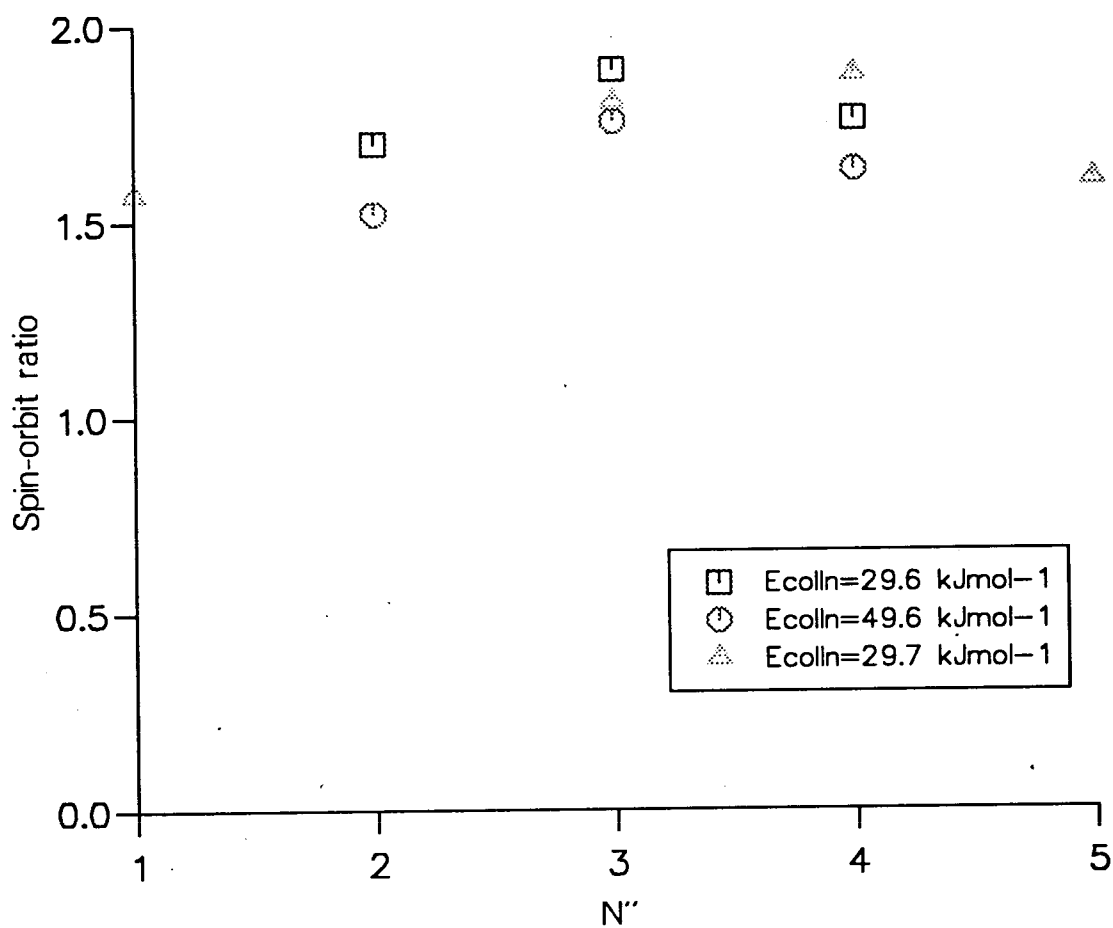


Figure 4-27: Plot of the ratio of the spin doublets ($^2\Pi_{3/2}/^2\Pi_{1/2}$), versus the rotational quantum number N'' . The points labelled with boxes or octagons denote results obtained in this work, while the triangular symbols denote results achieved by Luntz *et al*[2]. E_{colln} is the mean collision energy.

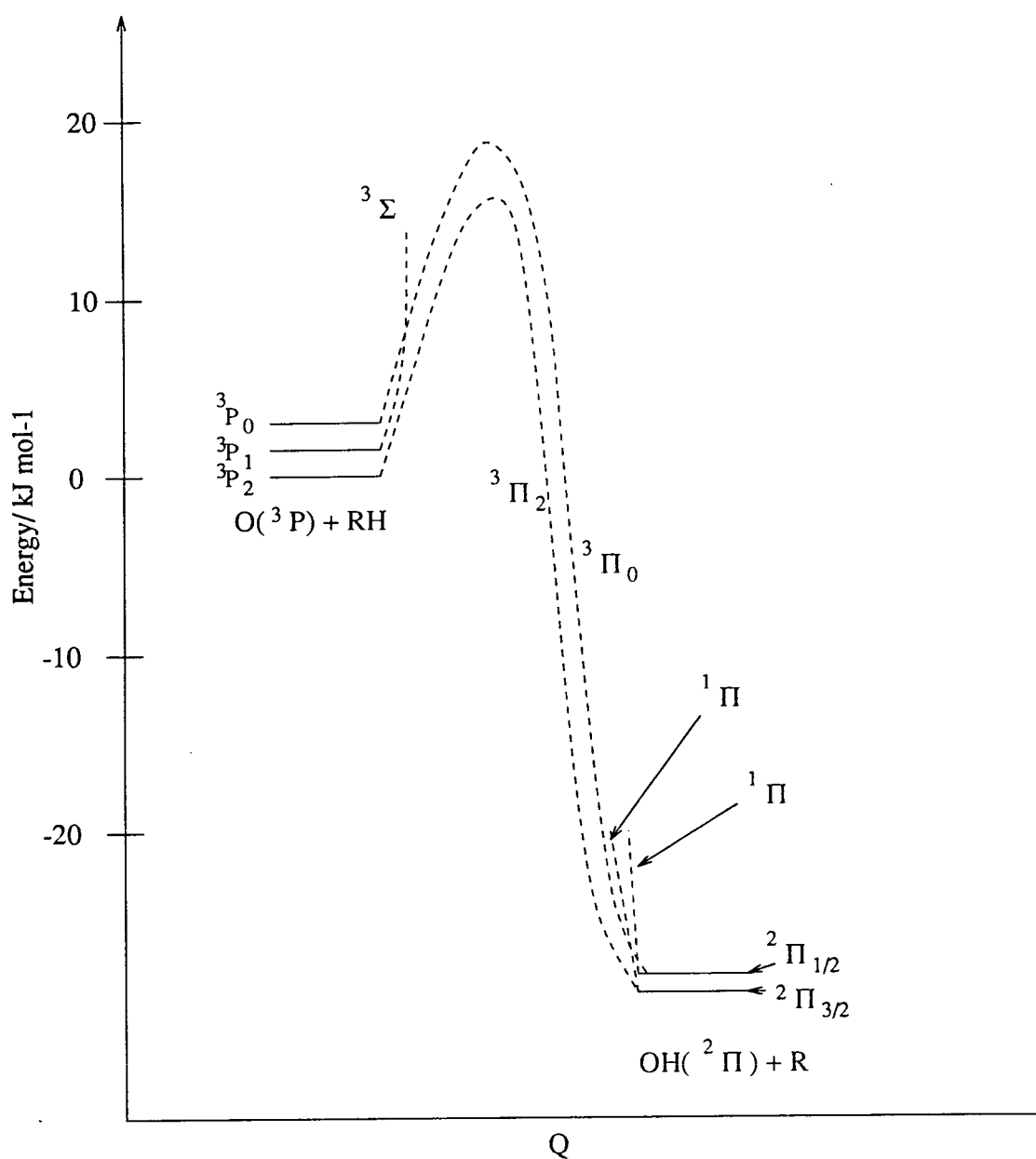


Figure 4-28: Schematic correlation diagram for the reaction $O(^3P) + RH \rightarrow OH + R$ including the spin-orbit surfaces. Q is the reaction coordinate. This figure was taken from reference[2].

and models to interpret the results from such experiments have been presented[26]. The origin of this selectivity is the conservation of the orientation of a single electron $p\pi$ orbital as the nuclei move from a transition state to products via an approximately planar fragmentation. The orientation of that orbital within the transition state is normally well defined, regardless of whether it is nonbonding, antibonding or bonding.

The main reason that Λ -doublets are of interest in reaction dynamics is that, for a $^2\Pi$ molecule such as OH, *for large values of the total angular momentum J* , there is an unpaired $p\pi$ electron lobe which lies perpendicular to the internuclear axis and is either parallel to $\mathbf{J}$ or alternatively in the plane of rotation of the molecule. The two Λ -doublet states are labelled A'' and A' , respectively, and represent the reflection symmetry of these two different directions of the unpaired $p\pi$ lobe. (The notation of Alexander *et al* [27] has been followed here which avoids the confusion which has previously arisen over the conflicting use of π^+ and π^- labels for these states.) When the OH product is not rotating the physical distinction between the Λ -doublets disappears and the ratio of Λ -doublet populations is unity.

Figure 4-29 shows the measured OH Λ -doublet population ratios $^2\Pi(A')/^2\Pi(A'')$, determined by comparing observed LIF intensities of main branch P lines (which probe A' states) to Q lines (which probe A'') states, for the reaction of $O(^3P) + \text{isobutane}$. The plot indicates no clear preference in the ratio of Λ -doublet components, with all the ratios approximating to unity. Andresen[26] has shown that for OH any preference in populating either of the Λ -doublet states can only occur for the higher rotational levels, typically $N''=15$. Since the reaction of $O(^3P) + \text{isobutane}$ has been shown to populate only to $N''=9$ it is not surprising that there is no selectivity in the Λ -doublet states. A separate *dynamic* point is that (regardless of the OH product state and the ability of spectroscopy to distinguish the Λ -doublets), the propensity for one Λ -doublet over the other can only arise if the geometry of the intermediate is *bent*, since otherwise no unique plane is defined (and A' and A'' are meaningless). Since the cold OH rotation results from a strongly collinear intermediate, it is again not surprising that no Λ -doublet propensity is observed.

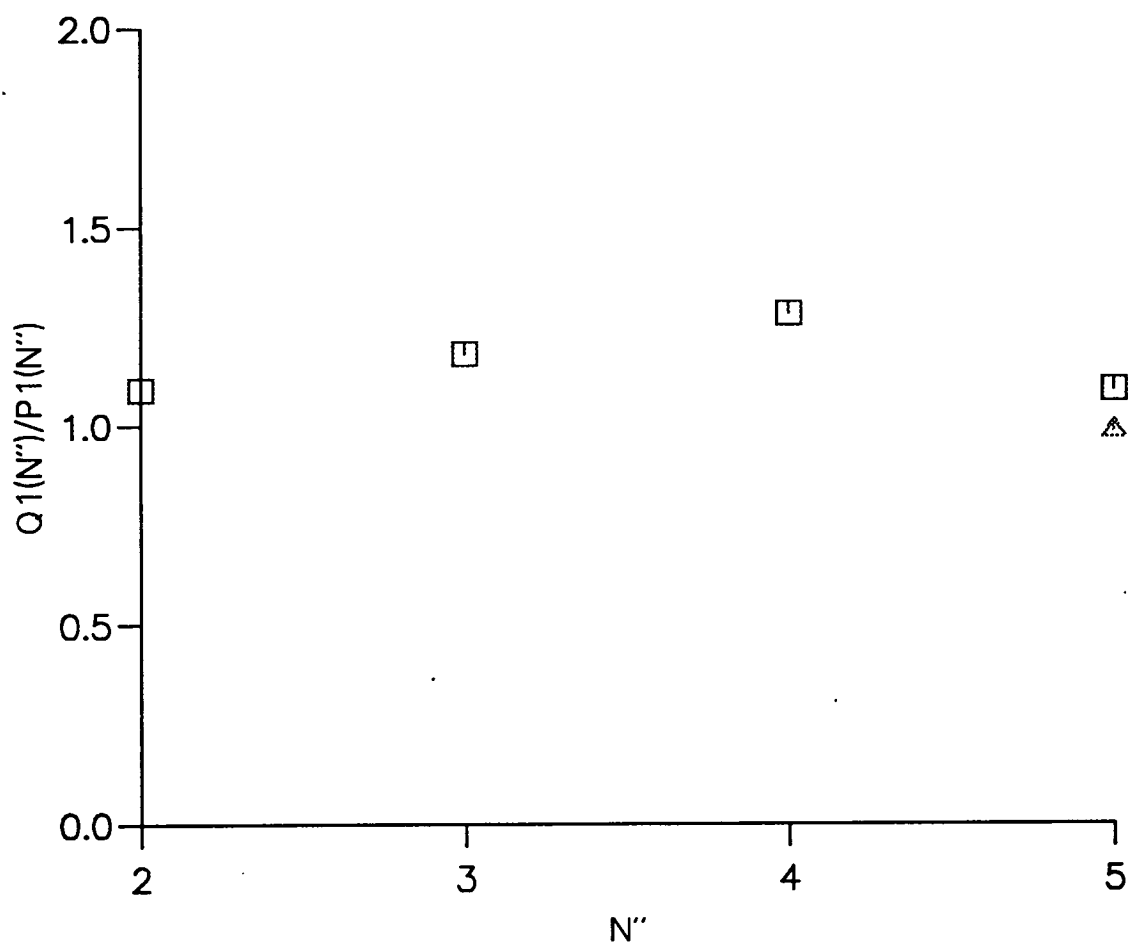


Figure 4-29: Plot of the ratio of populations $Q_1(1)/P_1(1)$ versus the rotational quantum number N'' to determine whether there is any selectivity in the population of Λ -doublet states resulting from the reaction of $O(^3P) + \text{isobutane}$. The box symbols represent measurements made at a photolysis wavelength of 337 nm, whereas the triangular point was made at 308 nm.

4.2.6 Conclusions

We have successfully repeated dynamical measurements on an important class of fundamental reactions using alternative and independent methods to those used in the original work of Luntz[2]. In general the results obtained agree with those of Luntz, where they are directly comparable.

A crude variation of the mean collision energy was possible through photolysing NO_2 at 337 nm and 308 nm. This was only found to have a significant effect on the $\text{O}(^3\text{P}) + \text{ethane}$ reaction where the $\text{OH}(v''=1)$ channel became energetically allowed.

The rotational distributions obtained for the different classes of $\text{O}(^3\text{P}) + \text{RH}$ reaction all led to very small partitioning of the available energy into rotation. This leads to the conclusion that the reactions are clearly dynamically rather than energetically controlled and are constrained to react through a collinear intermediate.

The spin-orbit measurements were in agreement with Luntz *et al*[2] even though the initial $\text{O}(^3\text{P}_J)$ distributions, produced by the photolysis of NO_2 , were significantly different from those produced by Luntz who employed a microwave discharge of O_2 . The results verify that reactions of $\text{O}(^3\text{P}) + \text{saturated hydrocarbons}$ lie nearer, but not in, the diabatic limit and that PES exit channel rather than entrance channel effects dominate.

The reactions populated rotational levels too low for there to be any preference in either of the Λ -doublet components of the OH product.

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Chapter 5

(2+1) REMPI Spectroscopy of HCl

5.1 Introduction

Hydrogen chloride is a molecule of fundamental interest in both chemistry and physics which lends itself to extensive theoretical and experimental investigation[1]. In the development of spectroscopy, gas phase kinetics and reaction dynamics, HCl has been a prototypical heteronuclear diatomic[2]. Many spectroscopic tools have been exercised in studies of HCl, incorporating a variety of conventional and laser light sources as well as synchrotron radiation.

The aim of this chapter was to carry out (2+1) REMPI studies on HCl. This was a necessary precursor to carrying out studies on reactions forming HCl as a nascent dynamical product. Although REMPI is a far more sensitive technique than, say LIF, in the sense of higher absolute sensitivity for a given concentration and in the absence of other interferences, it has been much less frequently used for population measurements. The reasons for this are twofold. Firstly there is a strong possibility of perturbations in the resonantly excited state because of the high density of electronic states reached with two or more UV photons. Secondly, there is the possibility of competition between dissociation and ionisation of the intermediate state which further complicates the state dependence of the ionisation rate.

The (2+1) REMPI spectrum of HCl in a conventional ionisation cell was first reported by Arepalli *et al*[3] in 1985. The spectrum was analysed in more detail by Callaghan *et al*[4] from measurements incorporating TOF mass resolution. This detection method has since been employed by several groups to enhance the sensitivity[5] [6][7][8] and concentrations as low as 10^5 molecules/cm³ have been

detected. Recently, an extensive REMPI study of HCl was reported by Green *et al* [9][10].

5.2 Electronic Structure of HCl

The hydrogen chloride $X^1\Sigma^+(0^+)$ ground state configuration, at its equilibrium geometry, is given by $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4(4\sigma)^2(5\sigma)^2(2\pi)^4$ or more concisely $\dots\sigma^2\pi^4$. Consequently, the simplest picture of HCl is to consider a molecular species with a $^2\Pi_i$ core and most excited states being Rydberg-like. Hence, such states converge to the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ ion limits and have vibrational and rotational constants similar to those of the corresponding ion[11]. The appropriate state labels simply follow the Hund's case (a) basis functions, that is, (Λ, S) coupling[11], where it is assumed that the interaction of the nuclear rotation with the electronic motion (spin as well as orbital) is very weak, whereas the electronic motion itself is coupled very strongly to the internuclear axis (see chapter 3 for definitions of angular momenta). The manifold of excited electronic states is expected to exhibit significant variation in angular momentum coupling, Rydberg~valence mixing, and charge-transfer character. For most states these features appear as a function of energy and internuclear distance [14]. Consequently, analyses of the excited state spectra has reflected these interactions in the form of electronic and vibrational as well as rotational perturbations. In particular, at high energies where states begin to experience medium to strong spin-orbit coupling, the rotational character is best described by Hund's case (c) basis functions, (Ω, ω) coupling, where only Ω is a good quantum number[11]. In (Ω, ω) coupling[15] there is a strong spin-orbit coupling in the core between the individual orbital and spin projection quantum numbers, λ_i and s_i for each of the π electrons to form separate ω_i . These ω_i then form a resultant Ω . This is then followed by a coupling of Ω with the angular momentum ω of the additional (Rydberg) electron. In practice it is found convenient to use both (Λ, S) and (Ω, ω) labelling schemes for the designation of electronic states.

Ginter *et al*[16][17][18][19] have proposed that the lowest lying configurations and corresponding electronic states for the hydrogen halides could be represented

in a general manner, as shown in table 5-1. In this table, the Rydberg states are labelled alphabetically according to the lowest energy first. In the left hand column of the table are listed the core electronic configurations along with Ginter's designation of the Rydberg electrons. In the right hand column of the table are listed the (Λ, S) term symbols for the derived electronic states. Listed in parenthesis for each term symbol is the total electronic angular momentum in the (Ω, ω) coupling scheme. The states are labelled in an alphabetical manner according to the lowest energy first. The following example explains the labelling for the promotion of the Rydberg electron to a σ orbital. In (Λ, S) coupling a σ -electron gives rise to a $^1\Pi$ and a $^3\Pi$ state. With increasing spin-orbit coupling the $^3\Pi$ state splits into 3 components with $\Omega=0, 1, 2$. In the (Ω, ω) limit the four states form two pairs, one with $\Omega=0, 1$ corresponding to the $^2\Pi_{3/2}$ ionisation limit, the other with $\Omega=1, 2$ corresponding to the $^2\Pi_{1/2}$ ionisation limit.

The additional V label attached to the $B^1\Sigma^+(0^+)$ state shown in the table was that originally used by Mulliken[20]. For consistency the V nomenclature will be followed in this chapter.

5.3 Two-Photon Spectroscopy

The excitation of HCl is characterised by two-photon electric dipole selection rules. Therefore, states described by Hund's case (a), (Λ, S) basis, are subject to a restriction on the change in axial component of the orbital angular momentum, $|\Delta\Lambda| \leq 2$. For Hund's case (c) coupling, there is a restriction on the change in the axial component of the total angular momentum, $|\Delta\Omega| \leq 2$.

Bray and Hochstrasser[21] have presented the basic theory of the two-photon selection rules and rotational linestrengths for a diatomic molecule. Their results can be used to calculate the linestrengths in the particular case where absorption occurs through a virtual state from an *isotropic* ground state. These results are a special case of the more generalised intensity formulae for an anisotropic sample later derived by Kummel, Sitz and Zare [22][23]. Since we are using ionisation techniques, direct application of the two-photon absorption formulae assumes that

Electronic Configuration	State
$...(\sigma^2\pi^4)$	$X^1\Sigma^+(0^+)$
$...(\sigma^2\pi^3)a\sigma^*$	$a^3\Pi_i(1,0_-), A^1\Pi(1)$
$...(\sigma\pi^4)a'\sigma^*$	$t^3\Sigma^+(1,0^-), V \text{ or } B^1\Sigma^+(0^+)$
$...(\sigma^2\pi^3)b\sigma$	$b^3\Pi_i(2,1,0^{+/-}), C^1\Pi(1)$
$...(\sigma^2\pi^3)c\sigma$	$d^3\Pi_i(2,1,0^{+/-}), D^1\Pi(1)$
$...(\sigma^2\pi^3)c\pi$	$e^3\Sigma^+(1,0^-), E^1\Sigma^+(0^+), f^3\Delta_i(3,2,1), F^1\Delta(2), g^3\Sigma^-(1,0^+),$ $G^1\Sigma^-(0^-)$
$...(\sigma^2\pi^3)d\pi$	$h^3\Sigma(1,0^-), H^1\Sigma^+(0^+), i^3\Delta_i(3,2,1),$ $I^1\Delta(2), j^3\Sigma^-(1,0^+), J^1\Sigma^-(0^-)$
$...(\sigma^2\pi^3)d\sigma$	$n^3\Pi_i(2,1,0^{+/-}), N^1\Pi(1)$
$...(\sigma^2\pi^3)a\delta$	$k^3\Pi_r(0^{+/-}, 1, 2), K^1\Pi(1), l^3\Phi(4, 3, 2), L^1\Phi(3)$
$...(\sigma^2\pi^3)e\sigma$	$m^3\Pi_i(2,1,0^{+/-}), M^1\Pi(1)$
$...(\sigma^2\pi^3)f\sigma$	$r^3\Pi_i(2,1,0^{+/-}), R^1\Pi(1)$

Table 5–1: General scheme for the lowest lying electronic states of the hydrogen halides (the configurations are meant to represent what may be no more than best estimates or largest contributions to the excited electronic state near the equilibrium internuclear separation). See text for labelling schemes.

the photoionisation cross section is a constant for any particular band and that there is saturation in the ionisation step. Consequently, in this discussion we are only concerned with ground state population and the cross sections resulting from the absorption of two photons of equal energy and the same polarisation.

5.4 Two-Photon Spectroscopy of HCl

The main purpose of this preliminary spectroscopic investigation was to identify electronic transitions from which reliable population information could be extracted. In concurrent dynamics studies employing REMPI-TOF detection of HCl molecules, three different electronic transitions have been used to monitor the population distributions, these have been the $E^1\Sigma^+(0^+) \leftarrow X^1\Sigma^+(0^+)$ [6][8], the $V^1\Sigma^+(0^+) \leftarrow X^1\Sigma^+(0^+)$ [7][27][24] and the $F^1\Delta(2) \leftarrow X^1\Sigma^+(0^+)$ [15][26] [27][28] [29]. We decided to carry out preliminary studies on all three states then decide on the best one to use for extracting populations. Figure 5-1 shows the relevant potential energy curves for the three states and the possible ionisation pathways. Figure 5-2 shows an energy level diagram for the three states.

5.4.1 Experimental

The main apparatus required to carry out a REMPI experiment was described in chapter 2. What follows is a brief description of the experimental procedure pertinent to the (2+1) REMPI of HCl.

UV laser light in the region 220-245 nm was produced via frequency mixing the 1064 nm fundamental light from the Nd:YAG laser with the doubled dye output of the dye laser. The final output beam was linearly polarised with an energy of approximately 1 mJ/pulse. This beam was focused by a 30 cm quartz lens into the reaction chamber, through Brewster-angled windows.

HCl gas (99.9% purity, Matheson) was purified via freeze-pump-thaw cycles in liquid nitrogen and was bled into the vacuum system via an adjustable needle valve through either the back flange of the reaction chamber or through a glass capillary, which allowed closer access to the ionisation region.

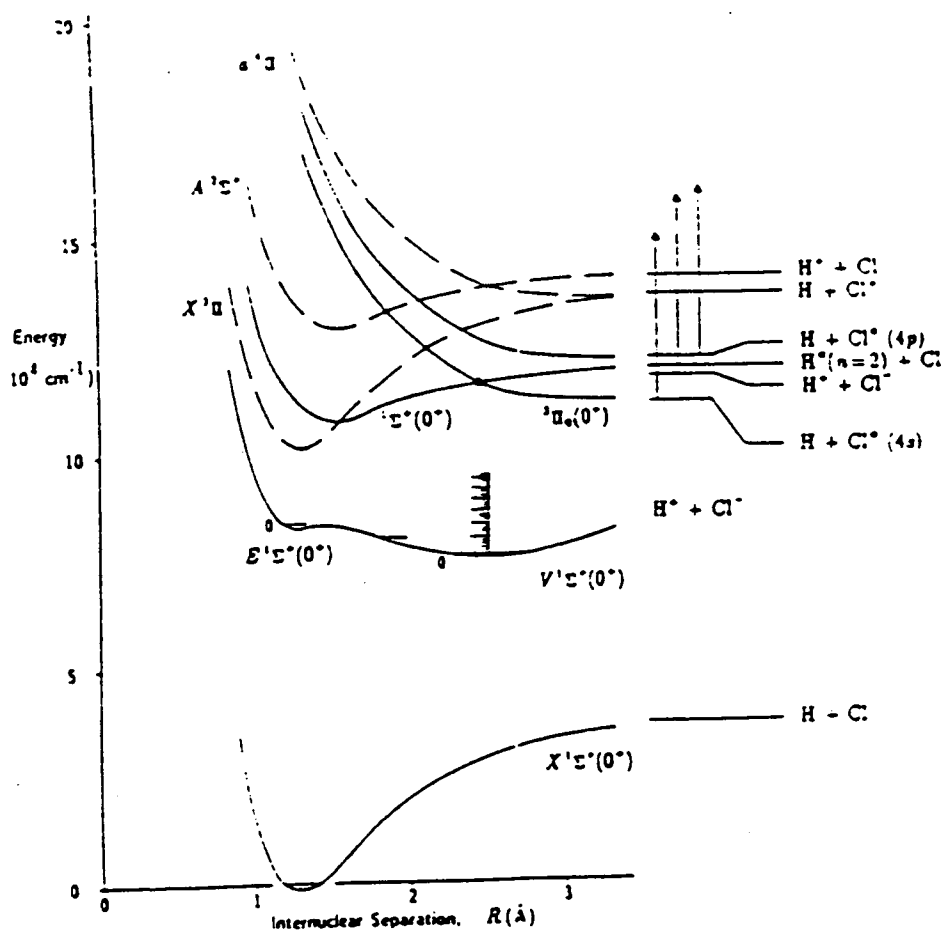


Figure 5-1: Selected potential energy curves for HCl and HCl⁺ from reference [10]. Vibrational levels of the V¹Σ⁺(0)⁺ state are indicated. An avoided crossing between the excited 1Σ⁺(0)⁺ and 3Π₀(0)⁺ states is indicated by a dot. The ionic states are distinguished by dashed lines.

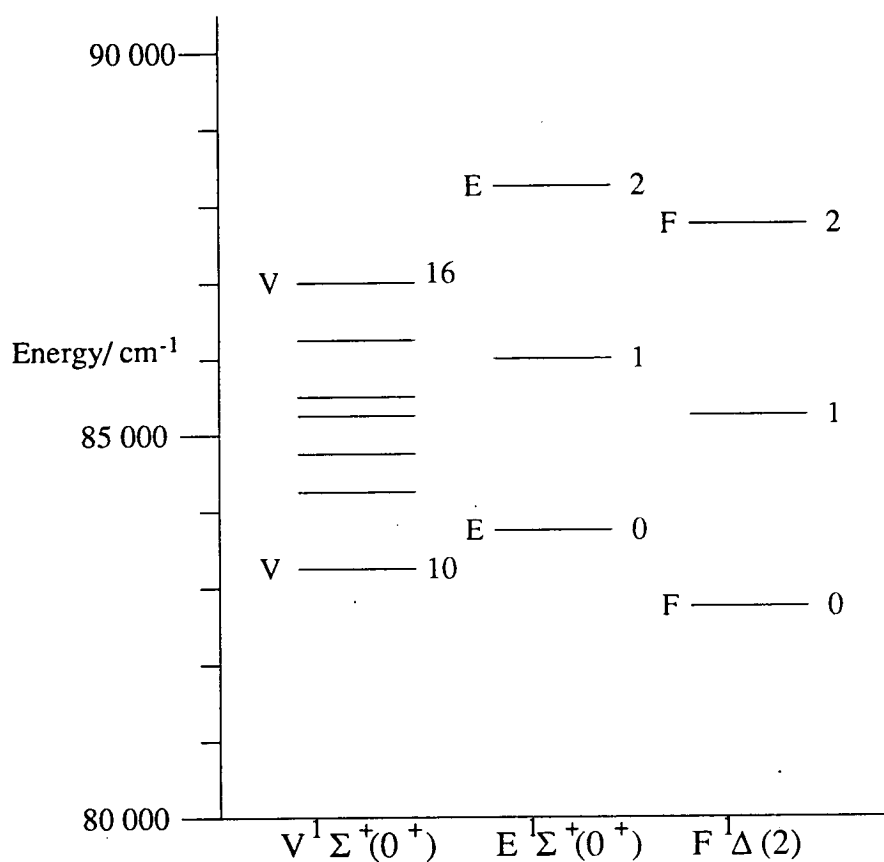


Figure 5-2: Vibrational energy level diagram for the states studied in this work. The solid lines indicate the position of band origins detected by (2+1) REMPI. Vibrational numbering and state label are provided alongside the lines. Taken from reference [10].

With gas flowing, typical pressures in the reaction and detection chambers were 1×10^{-5} mbar and 5×10^{-7} mbar, respectively.

All of these preliminary spectroscopic experiments were carried out at room temperature (approximately 300 K).

Mass resolved ion signals were collected from all isotopes of molecular (H^{35}Cl^+ , H^{37}Cl^+) and atomic (H^+ , $^{35}\text{Cl}^+$, $^{37}\text{Cl}^+$) species.

5.4.2 The $E^1\Sigma^+(0^+)$ State

The relatively unperturbed $E^1\Sigma^+(0^+)$ state is a Rydberg state and correlates to excited atoms. The selection rules for a $^1\Sigma-^1\Sigma$ 2-photon transition predict a strong Q-branch with very weak O and S branches. The E state ionises to produce both atomic (H^+ , $^{35}\text{Cl}^+$, $^{37}\text{Cl}^+$) and molecular (H^{35}Cl^+ , H^{37}Cl^+) ions. Although the mechanism for this process has not been confirmed, a plausible picture is that after absorption of 2 photons to the resonant intermediate level, absorption of a third photon results in competition between ionisation to produce the parent molecular HCl^+ ion, via the $X^2\Pi \leftarrow E^1\Sigma^+$ transition (see figure 5-1), and dissociation to produce excited neutral atoms (via any of the three transitions indicated by the arrows in figure 5-1). Absorption of a fourth photon by either of the Rydberg excited H or Cl atoms, from any of the dissociative potentials, can then yield either H^+ or Cl^+ ions.

Rohlfing *et al*[6] investigated the rotational energy transfer of $\text{HCl}(v'' = 1, J'')$ in collisions with a thermal bath of HCl. Rotationally selective excitation of $v'' = 1$ over $J'' = 1-6$ was achieved by stimulated Raman pumping, and the rotational relaxation from the initially pumped level was monitored via (2+1) REMPI through the Q-branches of the $E^1\Sigma^+(0^+) \leftarrow X^1\Sigma^+(0^+)$ (0-1) and (0-0) bands.

The relative REMPI Q-branch intensity for a $^1\Sigma-^1\Sigma$ transition for a linearly polarised laser can be written as

$$I [Q(J'')] \propto P_v(J'') S [Q(J'')] \quad (5.1)$$

where $P_v(J'')$ is the probability of the molecule being in rotational state J'' within the vibrational level v , $S [Q(J'')]$ is the two-photon linestrength for a $^1\Sigma-^1\Sigma$, Q-

branch transition, which can be written as[21]

$$S [Q(J'')] = 1 + \frac{J''(J'' + 1)}{5(2J'' - 1)(2J'' + 3)} \cdot R \quad (5.2)$$

where $R = (\mu_S^2/\mu_I^2)$ is a ratio of transition dipole factors, with μ_I and μ_S being the zero- and second-rank tensors, respectively.

Rohfling *et al* determined a value of $R = 0.52 \pm 0.06$ by examining the intensity of the O-branch relative to $Q(0)$, since

$$\frac{O(J'')}{Q(0)} = \frac{9J''(J'' - 1)}{20(2J'' - 1)} \cdot R \quad (5.3)$$

The transition chosen by Rohfling *et al* was not ideal for determining rotational populations, since the calculated intensities poorly matched the measured intensities for higher J'' levels. The rotational linestrength formulae were only reliable up to $J''=5$ for the Q-branch of the (0-0) transition and up to $J''=6$ for the Q-branch of the (0-1) transition. Large empirical correction factors had to be used to obtain population information from higher J'' levels. The same group suggested that the linestrengths fell off dramatically at the higher rotational levels because of a decline in the strength of the transition dipole with increasing rotational angular momentum.

Zare *et al*[8] used the (2+1) REMPI $E^1\Sigma^+(0^+) \leftarrow X^1\Sigma^+(0^+)$ (0-1) band to probe the $\text{HCl}(v=1, J)$ product from the reaction of $\text{Cl}(^2\text{P}_{3/2}) + \text{CH}_4$ ($\nu_3=1$, $J=1$) using the hot atom dynamics type experiment. This reaction only populates the lower rotational levels of the $\text{HCl}(v=1, J)$ product and in fact measurements were made on the $\text{HCl}(v=1, J=1)$ and $\text{HCl}(v=1, J=3)$ products only. Therefore, the diminished linestrengths associated with the higher rotational levels of the $E^1\Sigma^+(0^+) \leftarrow X^1\Sigma^+(0^+)$ transition did not apply. We planned to study reactions that produced HCl in higher rotational levels. Hence, we did not pursue transitions to the $E^1\Sigma^+(0)^+$ state any further.

5.4.3 The $V^1\Sigma^+(0^+)$ State

The $V^1\Sigma^+(0^+)$ state is an ion-pair state which correlates with H^+ and Cl^- ions. It has a large equilibrium internuclear distance ($r_e=2.512 \text{ \AA}$), compared to that of

the ground electronic state, resulting in broadly spaced rotational lines and long vibrational progressions. *Ab initio* calculations[32] [33] suggest that configuration mixing of the Rydberg $E^1\Sigma^+(0^+)$ state with the $V^1\Sigma^+(0^+)$ state, produces a state having minima at two different internuclear separations. The minimum at short HCl bond length results predominantly from the $E^1\Sigma^+(0^+)$ Rydberg state and the minimum at long HCl bond length correspondingly from the $V^1\Sigma^+(0^+)$ ion-pair state. The convention is to use the label $B^1\Sigma^+$ for this combined state having two minima.

The $V^1\Sigma^+(0^+)$ state ionises to produce both atomic and molecular ions in essentially the same way discussed for the $E^1\Sigma^+(0^+)$ state. However, the Cl^+/HCl^+ ratio is larger because of the increased Franck-Condon overlap at larger internuclear distances between the intermediate V state and the dissociative potentials at the 3-photon level.

As a result of other nearby $^1\Sigma^+$ Rydberg states, the $V^1\Sigma^+(0^+)$ state contains many bands which are perturbed. In particular, the $V^1\Sigma^+(v'=10)$ level is strongly perturbed by the $E^1\Sigma^+(v'=0)$ level, as is the $V^1\Sigma^+(v'=14)$ level by the $E^1\Sigma^+(v'=1)$ level (see figure 5-2). Consequently, these bands would not sensibly be used for probing HCl in dynamical studies.

Kay *et al*[7] measured the rotational distributions in $\text{HCl}(v''=0)$ produced by the rotationally inelastic scattering of HCl from the (111) surface of a single crystal of gold. The rotational distributions were measured using the $V^1\Sigma^+(v'=11,12,13) \leftarrow X^1\Sigma^+(v''=0)$ transitions. His analysis was much simplified by applying the following argument. Equation (5.2) can be rearranged to yield

$$S [Q(J'')] = \frac{(2J'' + 1)}{9} \mu_I^2 + \frac{(2J'' + 1)J''(J'' + 1)}{45(2J'' - 1)(2J'' + 3)} \mu_S^2 \quad (5.4)$$

S is dominated by the contribution from the zeroth order rank tensor, i.e. the first term in equation (5.3), so that $S/(2J'' + 1)$ is nearly independent of J'' . Equation (5.1) can now be simplified to

$$I = C P_v(J'') \quad (5.5)$$

where $C = \text{constant} = S/(2J'' + 1)$. For a Boltzmann sample

$$P_v(J'') = (2J'' + 1) \exp\left(\frac{-E_{rot}}{kT}\right) \quad (5.6)$$

where E_{rot} is the rotational energy of the ground state, k is the Boltzmann constant and T is the rotational temperature of the distribution. Therefore, the slope of a *weighted* least squares fit of $\ln \left[\frac{I}{2J''+1} \right]$ versus the rotational energy of the ground state yields the Boltzmann temperature of the sample.

Naaman *et al*[24] used the (2+1) REMPI $V^1\Sigma^+ \leftarrow X^1\Sigma^+$ (16-1) band of HCl to measure the rotational populations of the vibrationally excited HCl($v=1, J$) product produced in the photodissociation of C_2H_2 -HCl. The C_2H_2 -HCl complex was produced by expanding a mixture of HCl, acetylene and Ne through a molecular beam valve.

As a result of the simplified linestrengths, the Q-branch transitions of the V-X band systems seemed the most appealing candidates for extracting ground state rotational populations. We have carried out confirmatory experiments on the V-X ($v'=11-16$) band systems. Spectra for each band system were recorded for both the $^{35}Cl^+(m/e = 35)$ and the $H^{35}Cl^+(m/e = 36)$ ions simultaneously, so that Boltzmann plots using the total ion signal ($Cl^+ + HCl^+$) could be constructed.

All the figures that follow, showing V-X state spectra, were collected on the $H^{35}Cl^+(m/e = 36)$ mass channel. The wavelength referred to is the one-photon UV laser wavelength.

Figure (5-3) shows a room temperature (2+1) REMPI spectrum of the Q-branch of the V(11-0) transition. It's corresponding Boltzmann plot is shown in figure (5-4), which yielded a rotational temperature of $295 \pm 10K$, and is satisfactorily linear. Therefore, the V(11-0) band would be suitable for extracting ground state rovibrational populations.

Figures (5-5) and (5-6) show the Q-branch of the V(12-0) band and it's corresponding Boltzmann plot. The Boltzmann plot yielded a rotational temperature of $238 \pm 29K$. This is slightly below the expected room temperature value, therefore if the V(12-0) band were to be used for extracting populations then a set of correction factors would have to be applied which fitted the experimental data to a known Boltzmann distribution.

Figure 5-7 shows the Q-branch of the V(13-0) band. The absence of rotational

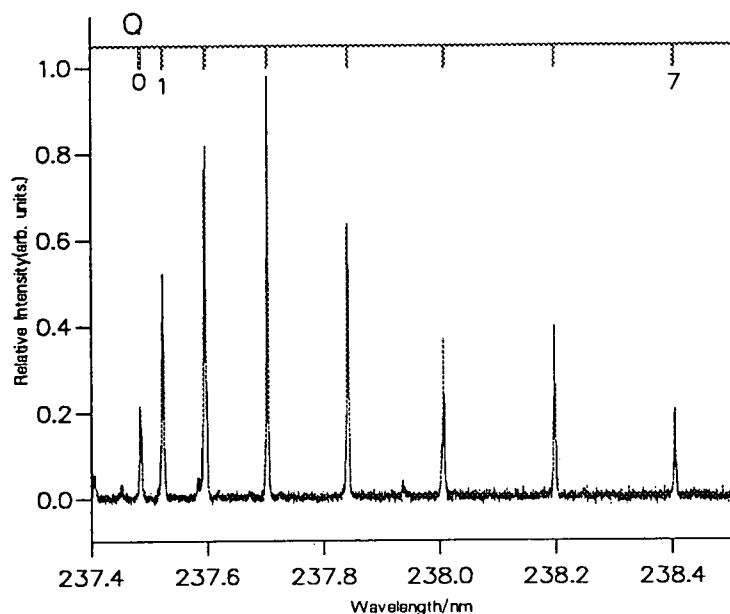


Figure 5-3: (2+1) REMPI spectrum of HCl taken at room temperature, showing the Q-branch of the V(11-0) band.

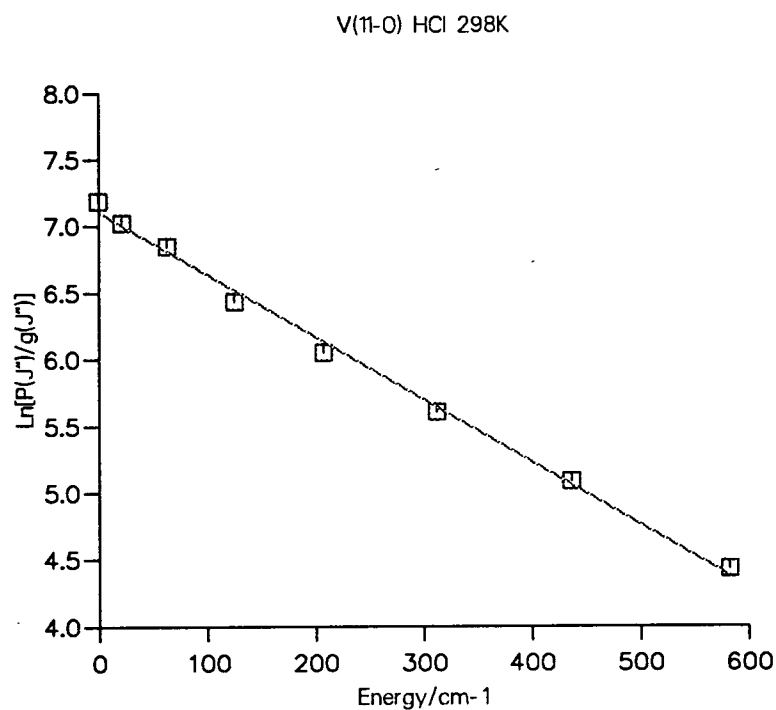


Figure 5-4: Boltzmann plot of $\ln(P(J'')/g(J''))$ versus the rotational energy of the ground state for the Q-branch of the V(11-0) band, where $P(J'')$ is the ground state population and $g(J'')=2J''+1$.

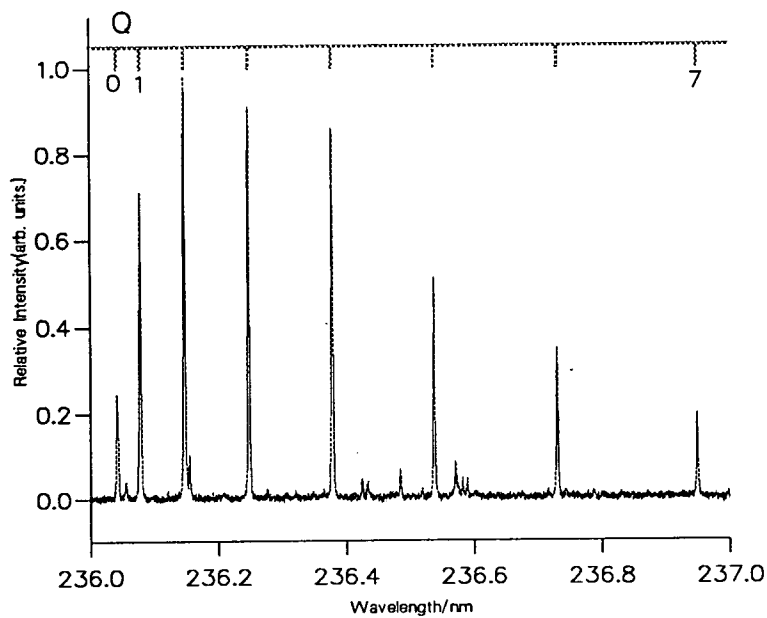


Figure 5-5: (2+1) REMPI spectrum of HCl taken at room temperature, showing the Q-branch of the V(12-0) band.

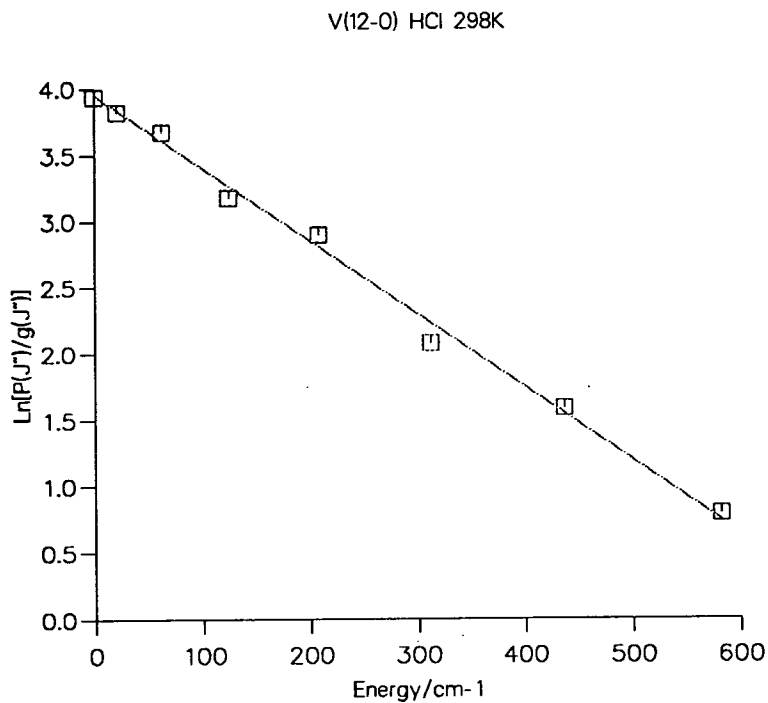


Figure 5-6: Boltzmann plot of $\ln(P(J'')/g(J''))$ versus the rotational energy of the ground state, for the Q-branch of the V(12-0) band.

lines higher than $J'' = 3$ is due to heavy energy perturbing[9]. The V(13-0) transition is therefore not a suitable transition for extracting populations.

No attempt was made to observe the V(14-0) band, since it is well known to be even more heavily perturbed than the V(13-0) band.

The Q-branches of the V(15-0), V(16-0) bands and their corresponding Boltzmann plots are shown in figures (5-8) to (5-11). The respective Boltzmann plots yielded rotational temperatures of $207 \pm 14\text{K}$ for the V(15-0) and $222 \pm 22\text{K}$ for the V(16-0). Correction factors would therefore have to be applied to both bands, as described above for the V(12-0) band.

5.4.4 The $F^1\Delta(2)$ State

The $F^1\Delta(2)$ state is a pure Rydberg state with a nominal $(X^2\Pi_{1/2})4p\pi$ configuration. It has an r_e value of $1.289\text{\AA}$ resulting in closely spaced rotational lines. It also implies that the $F^1\Delta(2)$ state has a strong Franck-Condon overlap with the $X^2\Pi$ molecular ion state, giving rise to parent molecular ions only from the REMPI process. This is demonstrated in figures (5-12) and (5-13), which show the (2+1) REMPI spectrum over the V(13-0) and F(0-0) transitions. Figure (5-12) was collected on the $\text{HCl}(m/e = 36)$ mass channel and shows the presence of both the V and F transitions. Figure (5-13) was collected on the $\text{Cl}(m/e = 35)$ mass channel and shows the absence of the F state transition, verifying that F state transitions result in the parent molecular ion only.

In the low J'' limit the selection rules and rotational linestrengths for a $\Omega = 0 \rightarrow \Omega = 2$ transition[21] predict strong Q- and R-branches of approximately equal intensities, a P-branch with approximately half the intensity of either the Q- or R-branches, and weaker O- and S-branches.

While the above properties make the transitions to the $F^1\Delta(2)$ state seem attractive for population studies, careful attention must be given to possible perturbations in the line intensities. Extensive work has been carried out recently by Gordon *et al* [25][26] [27][28] [29][30], in which REMPI was used to measure the nascent quantum state distributions of HCl produced in unimolecular reactions. In one of these studies[26] vinyl chloride was photodissociated by a 193 nm laser,

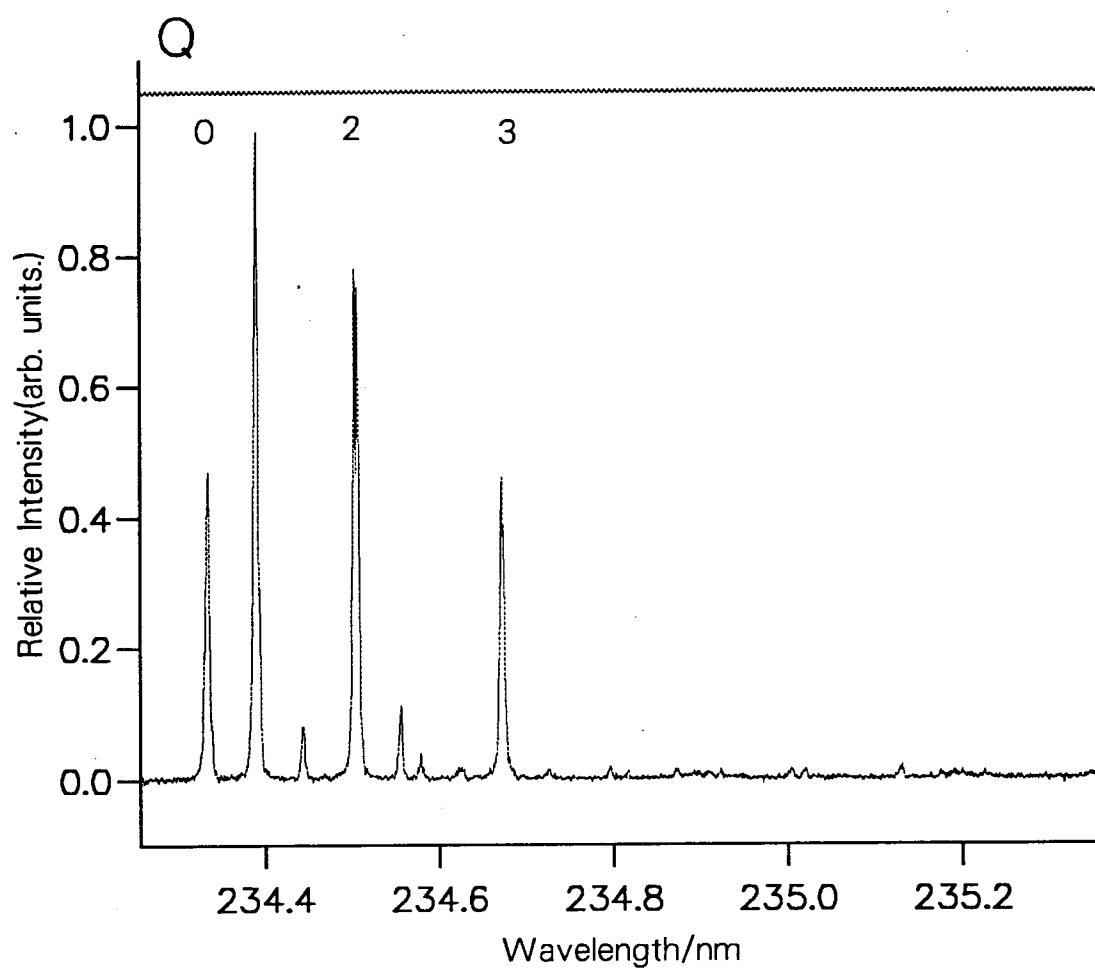


Figure 5-7: (2+1) REMPI spectrum of HCl taken at room temperature, showing the Q-branch of the V(13-0) band.

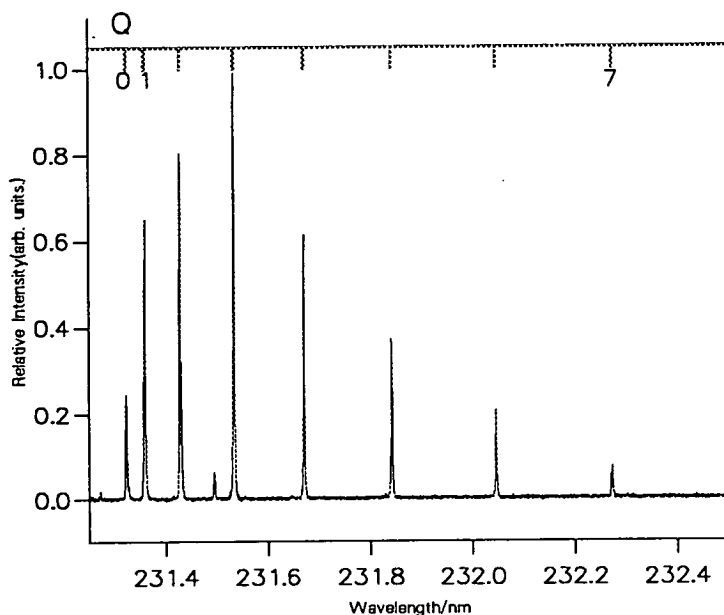


Figure 5-8: (2+1) REMPI spectrum of HCl taken at room temperature, showing the Q-branch of the V(15-0) band.

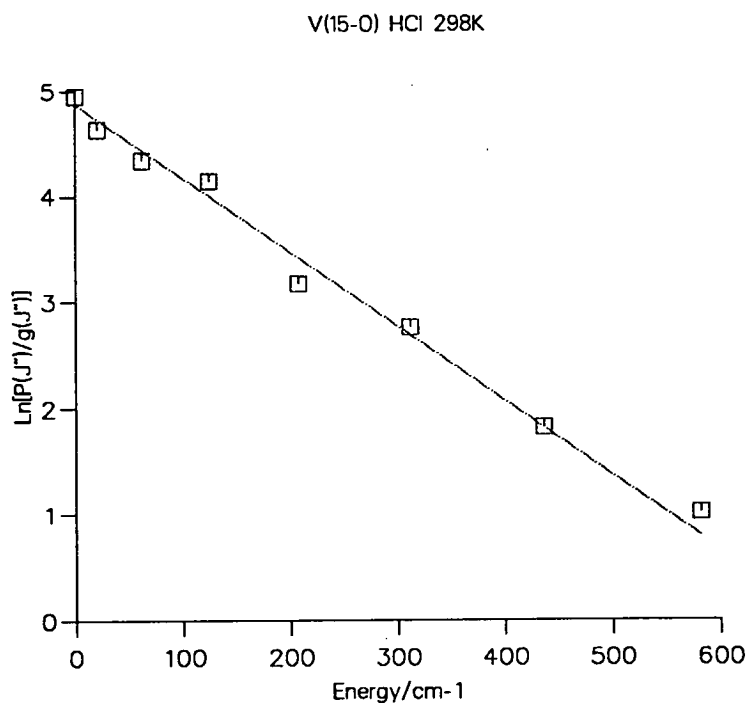


Figure 5-9: Boltzmann plot of $\ln[P(J'')/g(J'')]$ versus rotational energy of the ground state, for the Q-branch of the V(15-0) band.

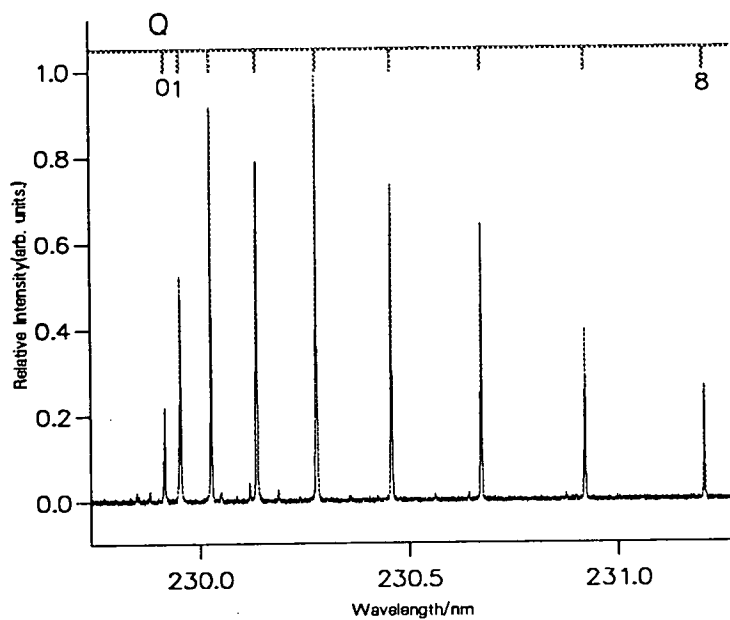


Figure 5-10: (2+1) REMPI spectrum of HCl taken at room temperature, showing the Q-branch of the V(16-0) band.

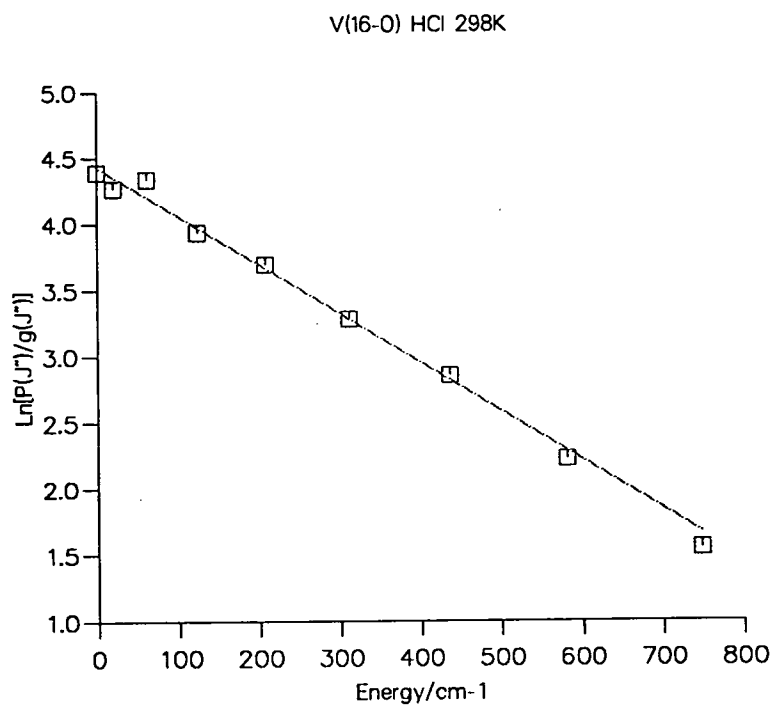


Figure 5-11: Boltzmann plot of $\ln(P(J'')/g(J''))$ versus rotational energy of the ground state, for the Q-branch of the V(16-0) band.

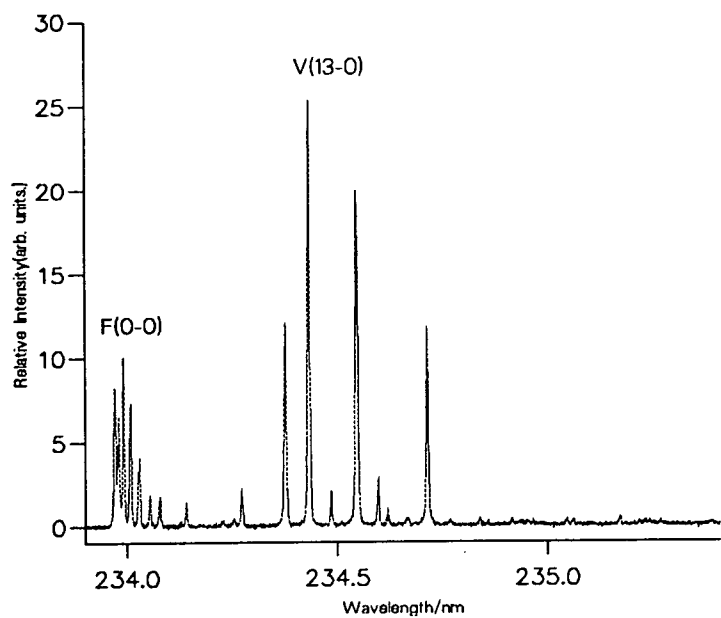


Figure 5-12: (2+1) REMPI spectrum of HCl at room temperature. Only the H^{35}Cl^+ ion signal is presented in the figure.

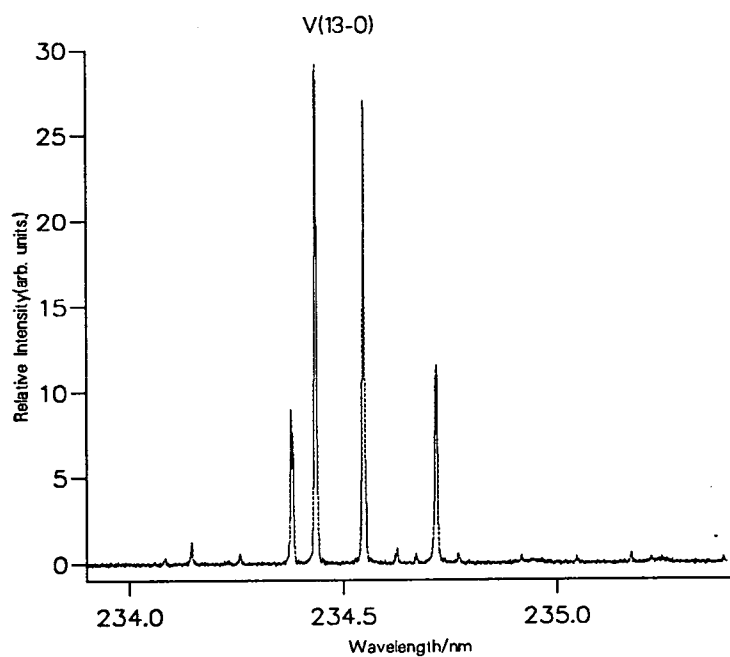


Figure 5-13: (2+1) REMPI spectrum of HCl at room temperature. Only the $^{35}\text{Cl}^+$ ion signal is presented in the figure.

producing, among other products, vibrationally and rotationally excited HCl. The REMPI spectra revealed an anomalous bimodal rotational structure in the F(0-0) and F(0-1) transitions. This structure could be due to either a bimodality in the nascent HCl state distributions or to perturbations in the spectrum. To determine whether the structure may be due to an anomaly in the spectrum, they remeasured the (2+1) REMPI spectra of the F(0-0) and F(1-0) transitions on a room temperature sample of HCl, so that room temperature Boltzmann plots could be constructed. They found that there was a striking concave curvature in the Boltzmann plots for all three branches (P, Q and R), between $J''=3$ to $J''=10$, with $J''=9$ being particularly weak. Hence, they could conclude that the anomalous rotational spectrum of vinyl chloride was caused by diminished linestrengths at intermediate J'' rather than by an anomaly in the population distribution. Previous studies failed to reveal this anomaly because of much lower populations for $J'' > 9$.

Several qualitative conclusions were drawn from their observations. First, there is strong evidence that the intensity loss between $J'' = 3$ and $J = 10$ is due to a perturbation of the resonantly excited $F^1\Delta(2)$ state at the two-photon level. The clearest indication of this is that the bimodal rotational structure was also observed in the F(0-1) transition. It is unlikely that the perturbation exists in an intermediate state that is reached with one-photon or in the ionising state which is reached with three photons, since the one and three photon energy levels for the (0-0) and (1-0) excitations differ by 1500 cm^{-1} . A further indication that the perturbation occurs at the two-photon level is that the deviations from the Boltzmann plots are the same for all three rotational branches. Gordon speculated that the intensity anomaly in the F(0-0) and F(0-1) transitions were a result of a perturbation of the $F^1\Delta(2)(v' = 0, 1)$ levels by some unobserved bound state. Arguments were presented suggesting that the perturbing state may be the $e^3\Sigma^+$ or $b^3\Pi_1$ states. The isolated perturbation of the Q(9) F(0-0) intensity appears to be the result of an interaction of the F state with the $g(0^+)$ state. Gordon *et al* have now verified these arguments[30] and have concluded that the intensity loss of the $F^1\Delta$ state is caused by spin-orbit perturbations by the predissociated $C^1\Pi(v'=2)$ and $b^3\Pi(v'=3)$ states. Because of the perturbations Gordon *et al* calculated a set of effective linestrength factors by fitting a static 300 K HCl (2+1) REMPI spectrum to

a known Boltzmann distribution. Consequently, the rotational distributions from the photodissociation of vinyl chloride could be corrected for, enabling dynamical information to be obtained.

We have carried out concurrent experiments which have confirmed the results obtained by Gordon *et al.* Figure (5-14) shows all five rotational branches for the $F(0-0)$ transition for a room temperature sample of neat HCl. The representative Boltzmann plot shown in figure (5-15) was constructed using the $R(1)$ to $R(7)$ lines from figure (5-14). It shows a curvature in the mid J'' rotational lines, in qualitative agreement with Gordon *et al.* Other work carried out by a colleague in this laboratory[31] established that although the deviations of the measured rotational linestrengths from the theoretical rotational linestrengths are the same for all branches, there are also discrepancies in the measured and theoretical linestrengths *between* branches. This point had not been commented upon elsewhere. The 2-photon rotational linestrength formulae of Bray and Hochstrasser[21] predict a $P(3)$ to $R(3)$ ratio of $\frac{1}{6}$, whereas experimental measurements gave a value of 0.3689. However, the deviations of the observed linestrengths from the theoretical values did remain constant over a wide range of experimental conditions, validating the use of rotational linestrength correction factors (these have been tabulated in reference [31]).

5.5 Conclusions

We have identified the $V^1\Sigma^+(0^+)(v'=11)$ level as the most reliable intermediate level for extracting ground state populations from (2+1) REMPI spectra of HCl.

The $V^1\Sigma^+(0^+)(v'=12)$ level and the $F^1\Delta(2)(v' = 0)$ level gave results with small and reproducible deviations from the expected linestrengths, enabling empirical rotational linestrength factors to be evaluated. Hence, either of these transitions would be suitable for obtaining population information.

The large, but reproducible, deviations from the expected line strengths given by the $(v' = 15, 16)$ levels of the $V^1\Sigma^+(0^+)$ state make transitions to these levels less attractive.

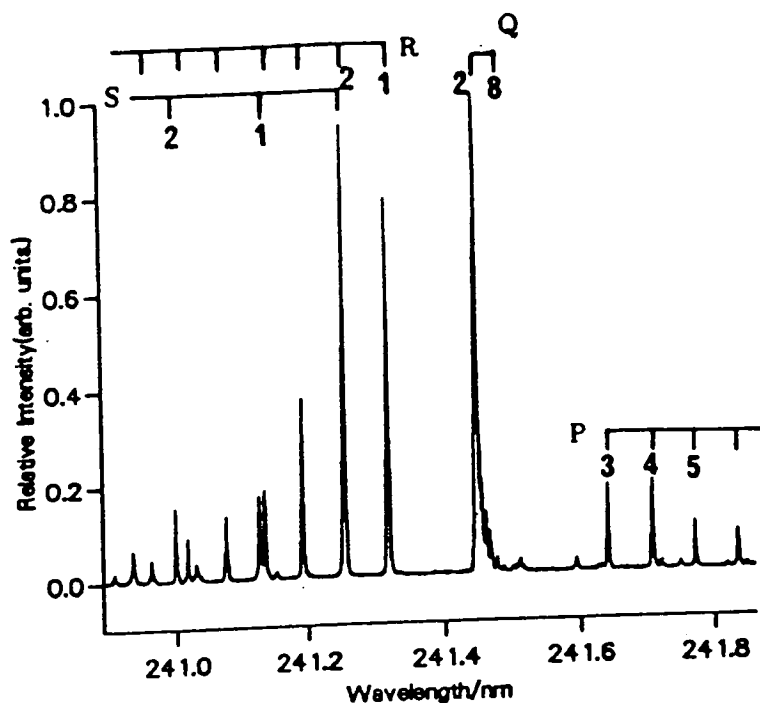


Figure 5-14: (2+1) REMPI spectrum HCl taken at room temperature, showing the O,P,Q,R and S-branches of the F(0-0) transition. This spectrum was recorded on the H^{35}Cl^+ ion channel.

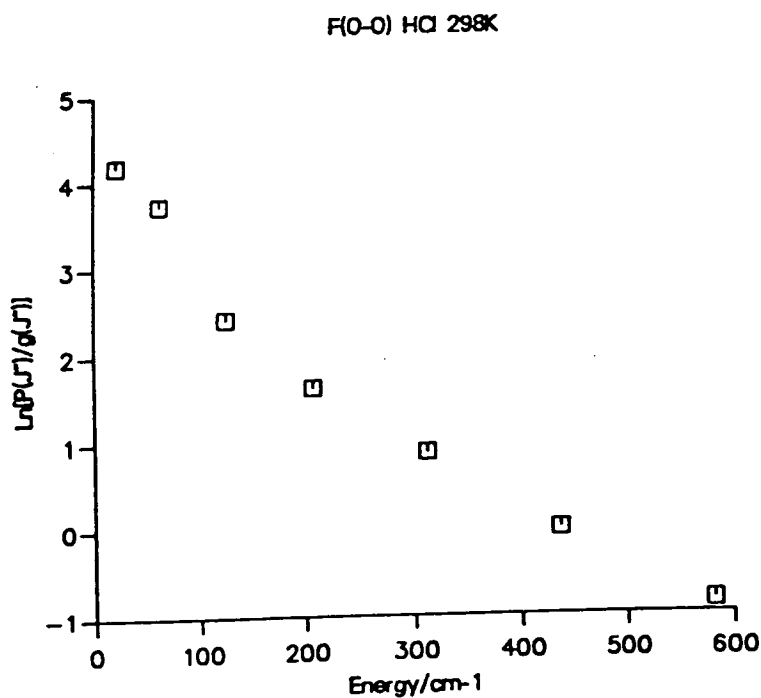


Figure 5-15: Boltzmann plot of $\ln P(J'')/g(J'')$ versus rotational energy of the ground state, using the R-branch of the F(0-0) band.

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Chapter 6

Effusive Source Dynamics of HCl

6.1 Introduction

For a substantial period of this thesis an independent photolysis laser was not available. During this period we performed preliminary dynamics experiments employing a microwave discharge for the production of atomic reagents. Our primary aim was to chemically generate rovibrationally excited HCl so that we could establish its REMPI spectroscopy for use in later-photolytic studies. We chose to produce rovibrationally excited HCl via the $\text{H} + \text{Cl}_2 \longrightarrow \text{HCl}^\dagger + \text{Cl}$ reaction (where the superior dagger is used to indicate rovibrational excitation of the ground electronic state).

The distribution of vibrational energy in the $\text{H} + \text{Cl}_2 \longrightarrow \text{HCl}^\dagger + \text{Cl}$ reaction was the first to be measured using the infrared chemiluminescence technique[1]. This involved the observation of the infrared emission from steady-state flow experiments and formed the basis of the first chemically pumped infrared laser. The $\text{H} + \text{Cl}_2$ reaction was studied using the measured relaxation method developed by Polanyi[2] in which the vibrational relaxation of the product molecules was obtained by recording infrared spectra at millisecond time intervals along the line of flow, at three observation windows in a cylindrical reaction vessel. These experiments were conducted at pressures slightly greater than 10^{-2} Torr, at which significant collisional vibrational relaxation could take place. Observation times were such that significant rotational relaxation also occurred. It was, nonetheless, possible to measure and correct for this relaxation.

The first study in which the full rovibrational quantum state distributions were measured for the $\text{H} + \text{Cl}_2$ reaction were reported by Polanyi in the early

Rate/cm ³ molecule ⁻¹ s ⁻¹	ΔH_0 /kJmol ⁻¹	E_a /kJmol ⁻¹
$2.19 \pm 0.32 \times 10^{-11}$	-189	7.5

Table 6-1: Thermodynamic and kinetic data for the H + Cl₂ reaction at 300 K, where ΔH_0 is the exothermicity of the reaction and E_a is the activation barrier. This data was taken from reference[5]

1970's[3][4], using the arrested relaxation (AR) method, where the vibrational and rotational relaxation was arrested by the rapid removal of excited products at a cold surface. These experiments also operated at much lower pressures than the measured relaxation experiments, typically 10⁻⁵Torr. The results achieved by Polanyi were rewarded with the Nobel prize for chemistry in 1986 and have served as a standard in experimental reaction dynamics.

Table 6-1 lists the relevant kinetic and thermodynamic data for the H + Cl₂ reaction at 300K.

Table 6-2 contains a summary of the measured energy disposal in the H + Cl₂ reaction. It shows the original results obtained by Polanyi, as well as confirmatory results achieved separately by other workers using the AR technique. The last row of measurements were the only results obtained at a non-thermal collision energy. Hydrogen atoms with translational energies of 0.45 eV were generated by thermal dissociation of molecular hydrogen in a tungsten tube. The increased total available energy has allowed vibrational levels up to $v'' = 6$ to be populated, although the fractional partitioning into vibration has decreased. The partitioning into rotation has increased at the enhanced collision energy.

Since our apparatus was not specifically designed for carrying out arrested relaxation measurements, we anticipated that the populations that we would observe may be significantly collisionally relaxed and that it was unlikely that we could replicate the nascent rovibrational distributions determined by Polanyi. However, as stated earlier, the main aim of this chapter was to essentially map out the REMPI spectroscopy of the higher vibrational levels of the ground electronic state of HCl. The accurate determination of nascent product distributions was to be

$\langle f_v \rangle$	$\langle f_r \rangle$	$N_v(1)$	$N_v(2)$	$N_v(3)$	$N_v(4)$	$N_v(5)$	$N_v(6)$	Ref.
0.38	0.08	0.12	0.44	0.40	0.04	-	-	[3]
0.40	0.10	0.11	0.42	0.43	0.04	-	-	[6]
0.39	0.08	0.19	0.43	0.30	0.03	0.01	-	[7]
-	-	0.13	0.39	0.39	0.09	-	-	[8]
0.33	0.11	0.25	0.28	0.24	0.13	0.07	0.03	[7]

Table 6–2: Summary of energy disposal for the $\text{H} + \text{Cl}_2$ reaction at 300 K, where $\langle f_v \rangle$ and $\langle f_r \rangle$ are the fractions of available energy appearing in vibration and rotation, respectively, and $N_v(v'')$ denotes the population of an individual vibrational level.

attempted via the more sophisticated hot atom type experiments at some future date when a photolysis laser might become available.

6.2 Choice of Electronic Transition to Probe $\text{HCl}^\dagger$

An appealing prospect for using the $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ transition in dynamical experiments, yielding vibrationally excited products, is that higher vibrational levels of the ground state have good Franck-Condon factors to the lower, isolated and therefore unperturbed levels of the resonant $B^1\Sigma^+$ state. We have calculated the Franck-Condon factors between the $X^1\Sigma^+$ and $B^1\Sigma^+$ states (using experimentally determined potentials from reference[9]) to identify the most favourable vibrational bands to probe the chemically produced, vibrationally excited products.

6.2.1 Calculation of Franck-Condon Factors

For a vibronic transition in absorption, the intensity is proportional to the square of the transition moment R_{ev} , and is independent of the transition frequency[10]

$$I_{abs} \propto R_{ev}^2 \quad (6.1)$$

In emission the expression is modified by a ν^3 term which arises because of the frequency dependence of the Einstein A coefficient

$$I_{em} \propto \nu^3 R_{ev}^2 \quad (6.2)$$

Explicitly, the Einstein A coefficient for a vibronic transition is given by [11]

$$A = \left[\frac{64\pi^4 \nu^3}{3hc^3} \right] R_{ev}^2 \quad (6.3)$$

The transition moment may be written as a product of the electronic transition moment R_e and the vibrational overlap integral $S_{v'v''}$

$$R_{ev} = R_e \cdot S_{v'v''} \quad (6.4)$$

Explicitly, denoting electronic and vibrational wavefunctions by ψ_e and ψ_v respectively, the two terms in the expression for R_{ev} are

$$R_e = \int \psi'_e \mu_e \psi''_e d\tau_e \quad (6.5)$$

where μ_e is the electric dipole moment operator, and

$$S_{v'v''} = \int \psi'_v \psi''_v dr \quad (6.6)$$

R_e is almost independent of r over the limited range of non-zero overlap. Thus, variations in the vibronic band intensities may be followed by evaluating $(S_{v'v''})^2$, the so-called Franck-Condon factor(FCF). The vibrational overlap integral is simply a measure of the extent to which the vibrational wavefunctions of the two vibronic levels overlap one another.

FCF's were calculated using a program written by K.P. Lawley[12]. Once the two potential energy functions for the two states involved were read into the program, the vibrational eigenvalues and eigenfunctions were then calculated using the Numerov-Cooley method[13] to solve the Schrodinger equation. FCF's for particular vibronic transitions were evaluated by numerical integration of the product of the relevant wavefunctions using Simpson's rule [14].

Plots of FCF versus resonant state vibrational quantum number, for each of the ground state vibrational quantum numbers, are shown in figures 6-1 to 6-4.

Plots are shown for $v'' = 1$ to 4, since these correspond to the excited vibrational levels most populated by the $\text{H} + \text{Cl}_2 \longrightarrow \text{HCl}^\dagger + \text{Cl}$ reaction. The FCF's calculated assume 1-photon absorption to the resonant excited state, therefore it is important to realise that they are not guaranteed to be quantitative, since in our case the B-X transition involves the absorption of two photons. For 2-photon transitions, there is the possibility of non-FC behaviour between the ground and resonant excited states. This arises because of real states in the vicinity of the 1-photon energy which invalidate the assumption that the only thing that matters is wavefunction overlap between the ground and resonant excited states. In conclusion, it is important to realise that the FCF's calculated are only meant to serve as a guide to the relative vibrational bandstrengths.

The most suitable $(v' - v'')$ B-X bands were chosen based upon

- the strength of the FCF
- whether the wavelength required for the particular $(v' - v'')$ band is obtainable with our laser system
- the resonant vibronic level is unperturbed

Figure 6-1 identifies the B-X(11-1) band as having the strongest FCF from $v''=1$. From section 5.4.3 we know that the $v' = 11$ intermediate resonant level is unperturbed and that the theoretical rotational linestrengths match those determined experimentally. The B-X(11-1) transition is easily accessed via two UV photons from our laser system.

Figure 6-2 identifies the B-X(10-2) band as having the strongest FCF from $v''=2$. However, the $v' = 10$ level of the B state is well known to be heavily perturbed. The next strongest transition is the B-X(9-2) band, however this has to be ruled out, since this transition requires a wavelength outwith the range of our laser system. This leaves the B-X(11-2) transition as the most suitable choice.

Similar arguments to the above led to the B-X(4-3) and B-X(7-4) bands being chosen to probe the $v'' = 3$ and $v'' = 4$ levels respectively.

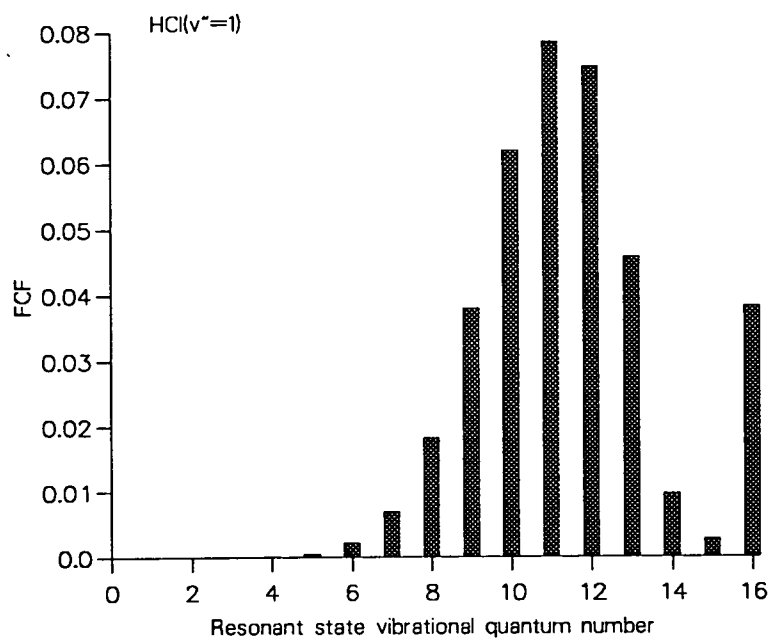


Figure 6-1: Franck-Condon factors for HCl $X^1\Sigma^+(v''=1)$ to HCl $B^1\Sigma^+(v'=0 \rightarrow 16)$

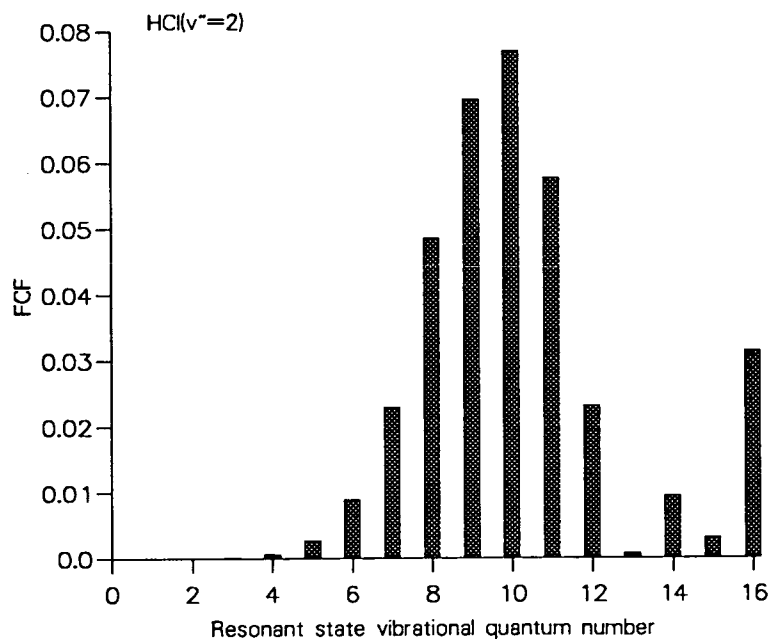


Figure 6-2: Franck-Condon factors for HCl $X^1\Sigma^+(v''=2)$ to HCl $B^1\Sigma^+(v'=0 \rightarrow 16)$

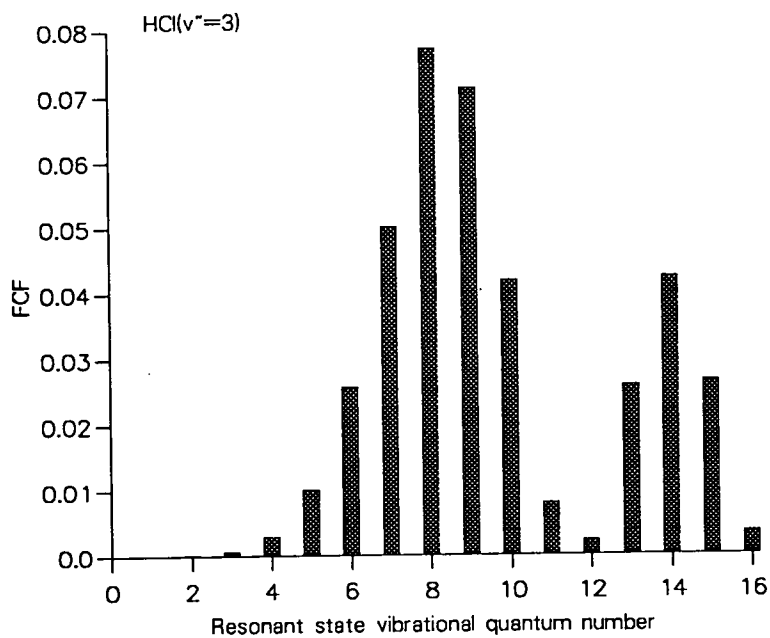


Figure 6-3: Franck-Condon factors for HCl $X^1\Sigma^+(v''=3)$ to HCl $B^1\Sigma^+(v'=0 \rightarrow 16)$

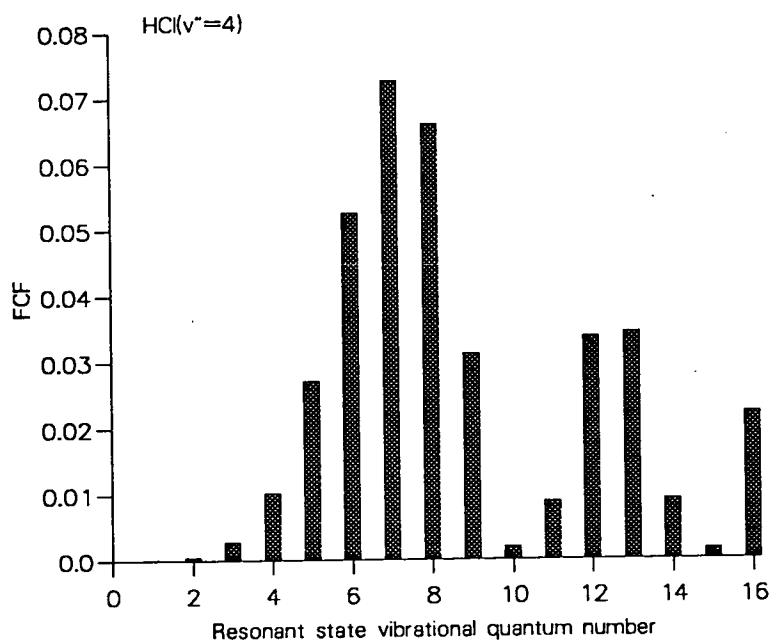


Figure 6-4: Franck-Condon factors for HCl $X^1\Sigma^+(v''=4)$ to HCl $B^1\Sigma^+(v'=0 \rightarrow 16)$

6.3 Experimental Procedure

The microwave discharge apparatus described in section 2.5.1 was used to carry out the following experiments. The reader is referred back to figure 2-7 which shows a schematic of the experimental apparatus used.

The first objective was to generate atomic hydrogen via the microwave discharge of molecular hydrogen in argon. The efficiency of the dissociation process could be monitored by observing the (2+1) REMPI of atomic hydrogen at 243.134 nm. This corresponds to the $2p\ ^2P_0 \leftarrow 1s\ ^2S$ transition[17] for atomic hydrogen and is shown in figure 6-5. This signal was extremely intense and if small changes in the efficiency of dissociation were to be observed it was important not to saturate the transition. The optimum gas mixture was found to be 50% H₂/50% Ar. The microwave power used depended on the pressure within the inner quartz discharge injector. Typical pressures in the discharge tube were 1-2 Torr, with corresponding powers in the range 15-50 Watts. Too high a microwave power led to overheating of the quartz discharge tube.

Recording the (2+1) REMPI spectrum of molecular chlorine served as a direct and convenient method of measuring the concentration of chlorine reaching the interaction region. Figure 6-6 shows the (2+1) REMPI spectrum of Cl₂ obtained at room temperature for the (5-0) band of the $2^1\Pi_g \leftarrow X^1\Sigma_g^+$ transition[18].

The REMPI detection of hydrogen atoms and chlorine molecules did not require unreasonably high densities at the gas-laser interaction region, therefore these preliminary experiments were carried out with the outer glass injector placed well out of the extraction fields. However, to ensure that detectable amounts of vibrationally excited HCl were being produced, it was necessary to create as high a pressure as possible at the gas-laser focus interaction region, to ensure frequent bimolecular collisions were being made between the atomic and molecular reagents. The laser focus position is fixed to ensure that the maximum number of ions are transmitted through the top hat hole (which separates the reaction and detection chambers). Therefore, the outer glass injector was moved into the extraction fields as close to the laser focus as possible. Placing such an insulator in a high electrical

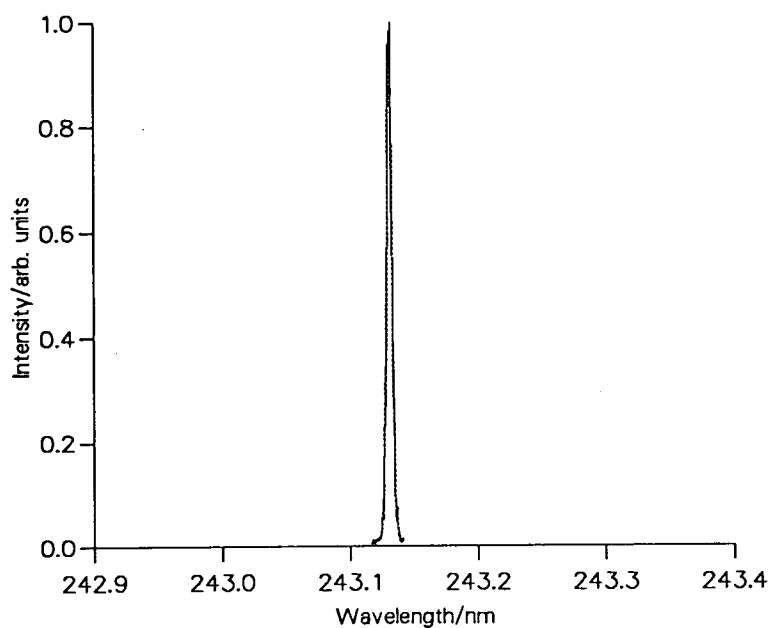


Figure 6-5: (2+1) REMPI spectrum of atomic hydrogen, showing the $2p^2\ P^0 \leftarrow 1s\ ^2S$ transition. The hydrogen atoms were generated by the microwave discharge of molecular hydrogen in argon.

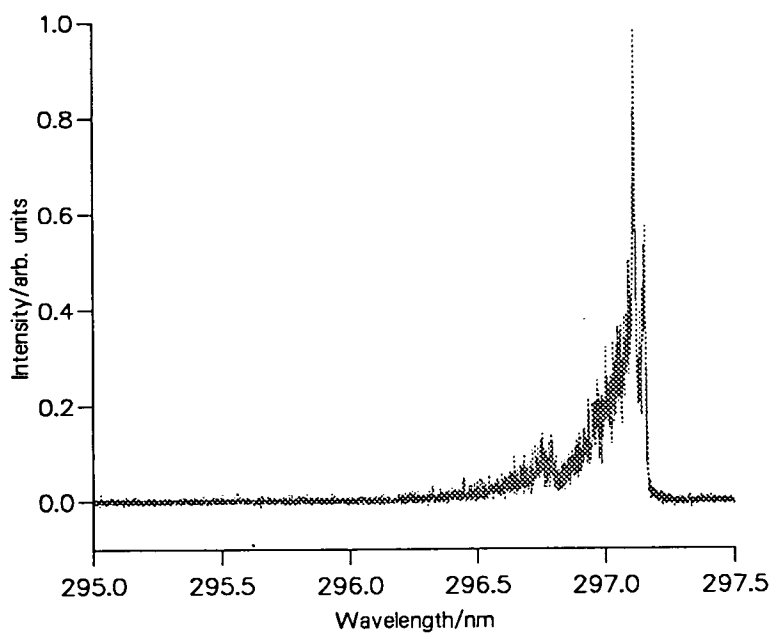


Figure 6-6: (2+1) REMPI of chlorine, obtained at room temperature for the (5-0) band of the $2^1\Pi_g \leftarrow X^1\Sigma_g^+$ transition. This spectrum was recorded for $^{35}\text{Cl}_2$

field creates a build up of charge on the outside surface of the injector. This was found to distort the electrical fields in the ion extraction region and subsequently led to reduced or complete loss of REMPI ion signals. Coating the bottom 5 cm of the outer glass injector with gold, which allowed it to be electrically floated, ensured greater homogeneity of the extraction fields and normal signal levels could be achieved. Gold was chosen because it is unreactive and should not generate unwanted reagent-injector surface reactions.

The first signs of any reaction between the hydrogen atoms and chlorine molecules taking place could be observed directly by watching the depletion of the (2+1) REMPI hydrogen atom signal on the addition of molecular chlorine. Detection of HCl in the ground vibrational state, generated by the reaction, could not be isolated from background HCl present in the Cl₂ sample, and not efficiently removed from the reaction chamber following its production in the H + Cl₂ reaction and subsequent relaxation in collisions with the walls. Therefore, to probe HCl generated by the reaction only, we decided to look for HCl produced in the higher vibrational levels.

Although the vibrational distributions listed in table 6-2 report the second and third vibrational levels as being the most populated levels, we decided to probe HCl in its first vibrational level. The reasoning behind this choice was that our apparatus contained no cold surfaces to remove excited products, as in the original AR experiments, and that we could therefore expect significant collisional deactivation of the higher vibrational levels via collisions with scattered background products, unreacted reagents and the walls of the injector.

As discussed in section 6.2.1 it was our original intention to look for any chemically produced HCl($v'' = 1$) via the B-X(11-1) transition. However, during the course of this work Gordon *et al*[15] reported the detection of HCl($v'' = 1$) via the $F^1\Delta(2) \leftarrow X^1\Sigma^+(1-1)$ transition. For initial detection and optimisation of HCl($v'' = 1$), the F-X(1-1) transition is a better choice than the B-X(11-1) transition since

- it is a more intense transition

- nearby $\text{HCl}(v'' = 0)$ rotational lines allow the $m/e = 36$ REMPI ion signal to be optimised for different injector-laser distances and corresponding injector voltages
- the rotational lines are closely spaced, making detection easier

The main disadvantage of using the F-X(1-1) transition is that the $v' = 1$ level of the $F^1\Delta(2)$ state is perturbed[15]. We hoped to optimise $\text{HCl}(v'' = 1)$ production whilst monitoring the F-X(1-1) transition, then proceed to map the unperturbed B-X(11-1) transition, which was to be used in later hot atom dynamics experiments.

6.4 Results and Discussion

Figure 6-7 shows an extended spectrum of the $F^1\Delta(2) \leftarrow X^1\Sigma^+(0-0)$ region taken at room temperature for a neat sample of HCl. The arrow points at the expected location of the Q-head of the F-X(1-1) band. This region is shown at higher resolution in figure 6-8, which was also obtained for a room temperature sample of neat HCl.

After a considerable amount of preliminary work into establishing uniform fields when the injector apparatus was moved into the extraction region, the first signs of any vibrationally excited HCl being produced are shown in figure 6-9. This spectrum was recorded with the outer injector 25 mm away from the laser focus and the inner injector 35 mm within the outer injector. The total pressure in the reaction chamber was 4×10^{-5} mbar. The $\text{HCl}(v'' = 1)$ signal was optimised using a higher flow rate for chlorine than for hydrogen (1.5 Cl_2 : H_2 : Ar). The microwave discharge was operated at 50 W, with the previously determined optimum gas mixture of 50% H_2 to 50% Ar. The $\text{HCl}(v'' = 1)$ signal was not found to be particularly sensitive to the microwave power, however it was found to be very sensitive to the position of the laser focus relative to the bottom of the injector where the excited products emerged from.

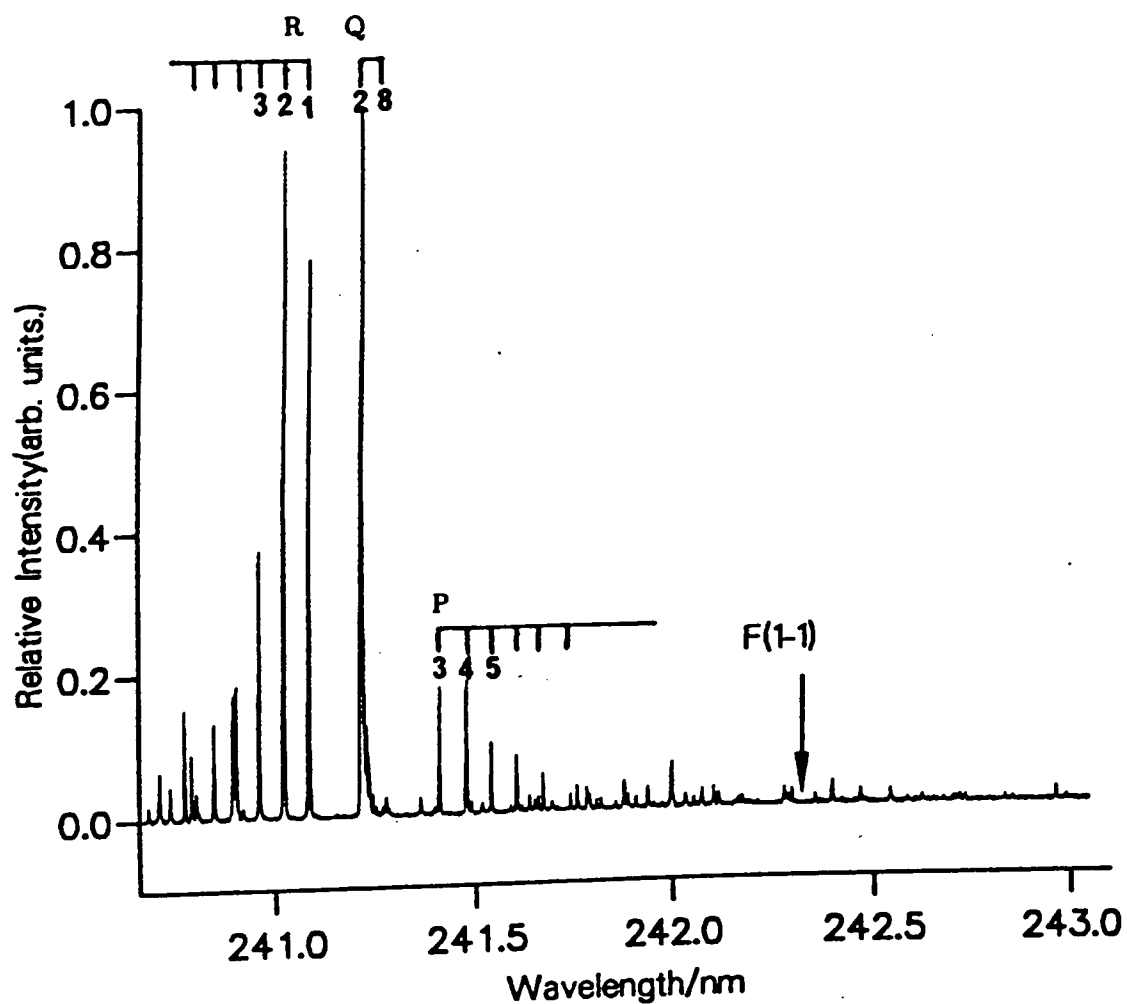


Figure 6-7: (2+1) REMPI of HCl taken at room temperature for a neat sample of HCl, showing the P-, Q- and R-branches of the $F^1\Delta(2) \leftarrow X^1\Sigma^+(0-0)$ transition and the expected location of the Q-head of the F(1-1) band.

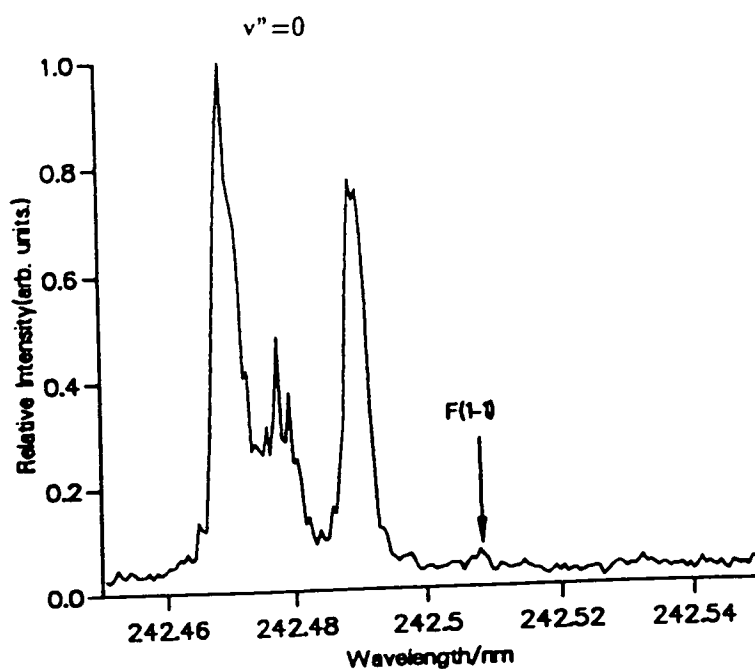


Figure 6-8: (2+1) REMPI of HCl taken at room temperature for a neat sample of HCl, showing a high resolution scan over the wavelength region where the Q-head of the F(1-1) band is expected

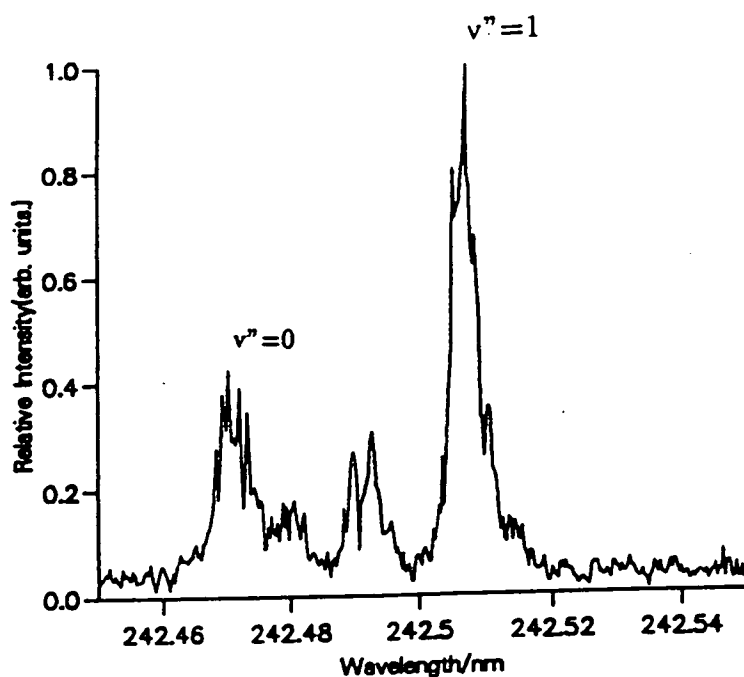


Figure 6-9: (2+1) REMPI of HCl taken over the Q-head region of the F(1-1) band, obtained via the $\text{H} + \text{Cl}_2$ reaction. This spectrum shows the first appearance of $\text{HCl}(v''=1)$.

Figure 6-10 shows an extended spectrum over the F(0-0) and F(1-1) regions, operating at a increased total pressure in the reaction chamber of 2.2×10^{-4} mbar. This was the maximum pressure possible operating with a 5 mm diameter orifice fitted in the top hat flange, separating the reaction and detection chambers. A higher pressure would lead to too high a pressure in the detection chamber resulting in damage of the microchannel plates. The 5 mm diameter orifice was chosen since it offered a good balance between allowing reasonably high pressures in the reaction chamber while still allowing high ion transmission from the reaction chamber through to the detector. Figure 6-10 shows that the Q-head of the F(1-1) transition is of about equal intensity to the P(3) line of the F(0-0) transition.

In the following optimisation procedures, any enhancement in the $\text{HCl}(v'' = 1)$ signal was observed by comparing the ratio of the Q(2) line of the F(1-1) transition with the neighbouring $\text{HCl}(v'' = 0)$ peaks.

First of all, the effect on the $\text{HCl}(v'' = 1)$ signal size as a function of the distance the inner injector was within the outer injector was investigated. Figure 6-11 shows a series of spectra taken over the F(1-1) Q-head wavelength region at three different inner-outer injector distances of 0, 35 and 50 mm. These spectra were all recorded operating at a total gas pressure of 2.2×10^{-4} mbar with the outer injector 25 mm away from the laser focus. The reduced $\text{HCl}(v'' = 1)$ signal obtained by operating with the injectors level (0 mm) can be attributed to short residence times in the reaction region for the hydrogen atoms, leading to infrequent collisions with chlorine molecules. Conversely, when the hydrogen atoms spend more time within the reaction region (as in the middle spectrum of figure 6-11) they are given a greater opportunity to react with chlorine molecules, to form vibrationally excited HCl. The bottom spectrum shown in figure 6-11 shows that the $\text{HCl}(v'' = 1)$ signal decreases slightly on moving the inner injector even further up within the outer injector. This is because the number of deactivating collisions that the newly formed vibrationally excited species encounters, before being detected, has increased.

The next series of spectra, shown in figure 6-12, demonstrate the effect on the $\text{HCl}(v'' = 1)$ signal on moving the outer injector further down into the extraction field towards the laser focus. The outer injector was carefully moved down 1 mm

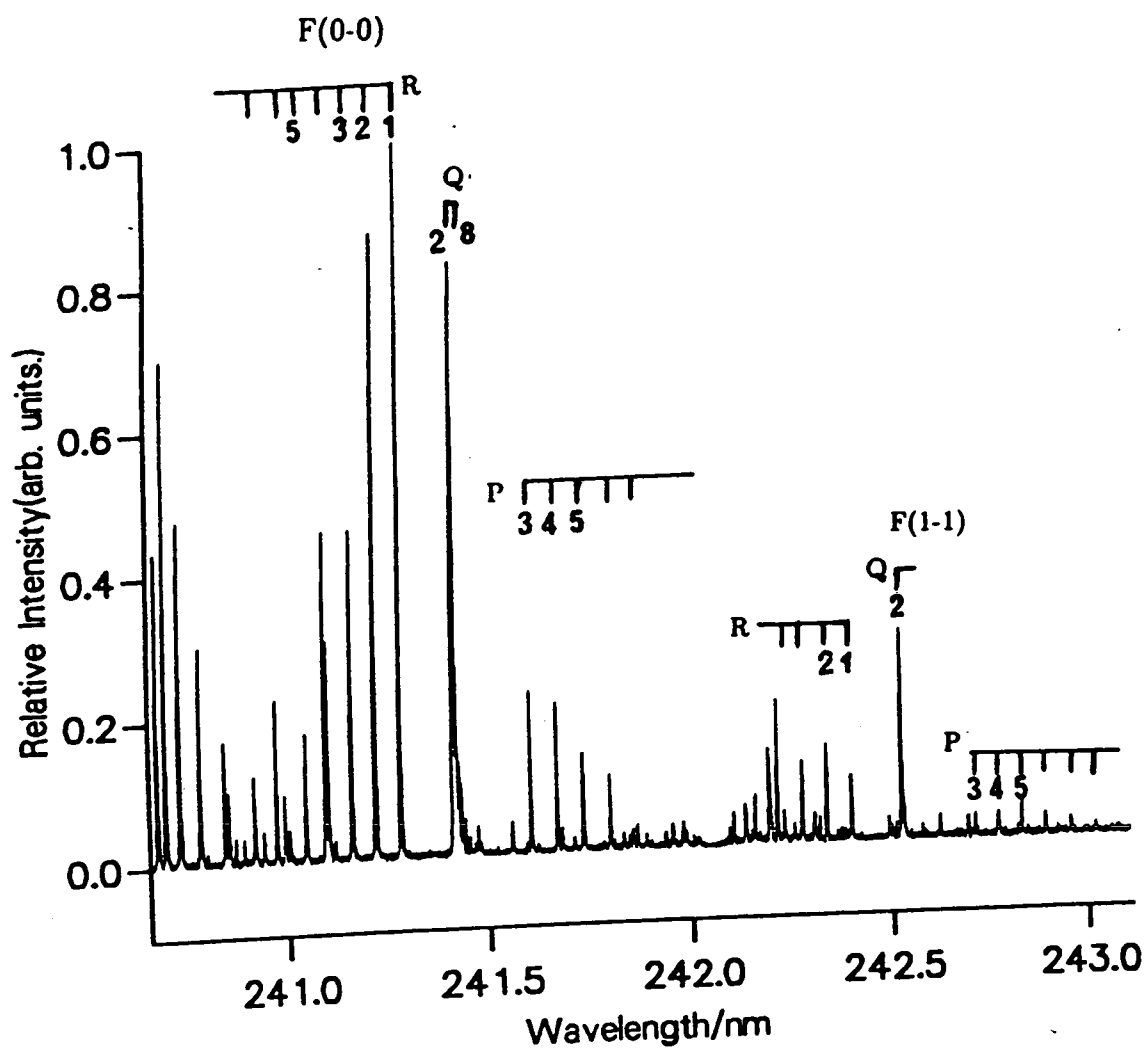


Figure 6-10: (2+1) REMPI of HCl obtained via the $\text{H} + \text{Cl}_2$ reaction. This spectrum shows the P-, Q- and R-branches of both the F(0-0) and F(1-1) bands.

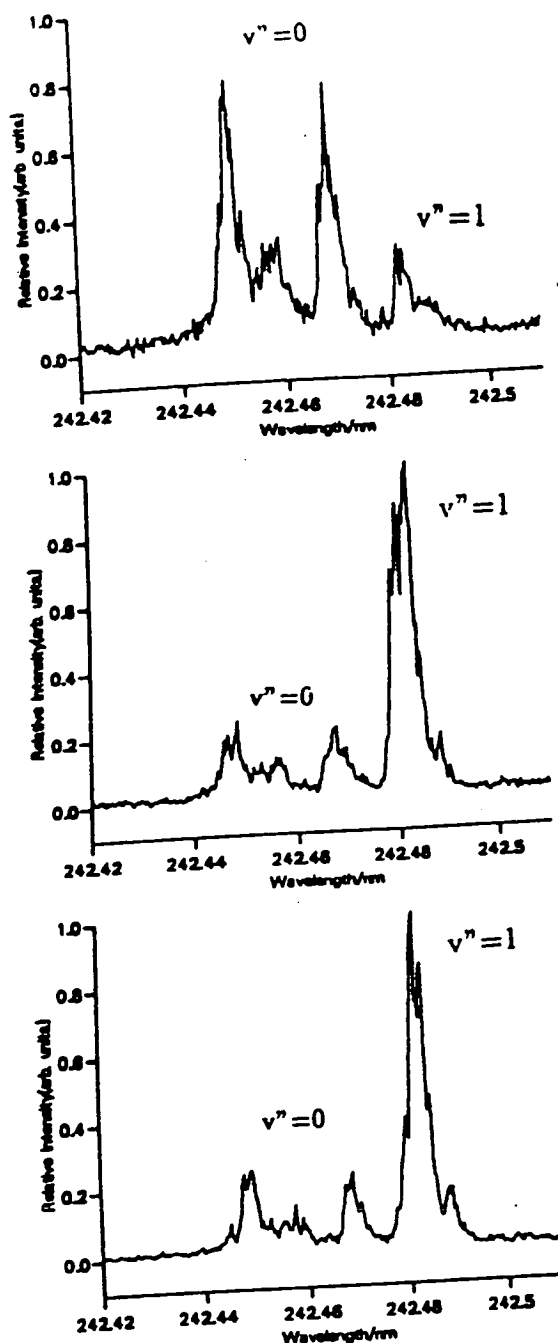


Figure 6-11: The sequence of spectra shown in this figure were recorded to demonstrate the effect on the $\text{HCl}(v''=1)$ signal on moving the inner injector further up within the outer injector. The top, middle and bottom spectra were obtained for outer-inner injector distances of 0 mm, 35 mm and 50 mm respectively. The outer injector was kept at a constant distance of 25 mm away from the laser focus.

at a time, after which the $\text{HCl}(v'' = 1)$ signal was reoptimised by altering the injector voltage. When the outer injector was 25 mm away from the laser focus the $\text{HCl}(v'' = 1)$ signal remained constant for a specific injector voltage of ~ 1800 V and could be set within 50 V, whereas when the injector was only 5 mm from the laser focus the $\text{HCl}(v'' = 1)$ signal became far more sensitive to the voltage on the injector and had to be set within 5 V. The injector could not be moved closer than 5 mm from the laser focus, as the $\text{HCl}(v'' = 1)$ signal became unstable.

The spectra shown in figure 6-12 show that the $\text{HCl}(v'' = 1)$ signal clearly increases as the outer injector is brought closer to the laser focus. This is hardly surprising since the local gas density of "hot" gases emerging from the injector relative to background gas in the chamber at the laser focus region will have increased.

To increase the $\text{HCl}(v'' = 1)/\text{HCl}(v'' = 0)$ ratio further, the only remaining option was to adjust the flows of hydrogen and chlorine. Higher flows could be tolerated by opting for a smaller orifice diameter in the top hat flange, to increase the pressure differential between the reaction and detection chambers. Although space charging is more likely at higher pressures, the gentler focusing conditions achieved with the 50 cm focal length focusing lens should compensate for the increase in pressure.

The 5 mm diameter orifice was replaced with a 2 mm diameter one. This allowed a maximum pressure of 2 mTorr in the reaction chamber, while maintaining the necessary pressure of 1×10^{-6} mbar in the detection chamber. Therefore by changing the orifice size an approximately 10-fold increase in the maximum permissible pressure was achieved, implying a 100-fold increase in the total rate of collisions, was found, as expected, to have a significant effect on the $\text{HCl}(v'' = 1)$ production. Figure 6-13 shows the optimum production of $\text{HCl}(v'' = 1)$ achieved, operating at a total pressure of 2 mTorr (1mTorr each of Cl_2 and H_2/Ar). In figure 6-10, which showed a spectrum over both the F(0-0) and F(1-1) regions before much optimisation of the $v''=1$ signal was made, the ratio of the Q-head of the F(0-0) transition to the Q-head of the F(1-1) transition was ~ 5 . Since the ratio of the Q-head of the F(0-0) transition to the small $v''=0$ peaks near the Q-head of the F(1-1) transition is a constant, then comparing the ratio of the the Q-head of the

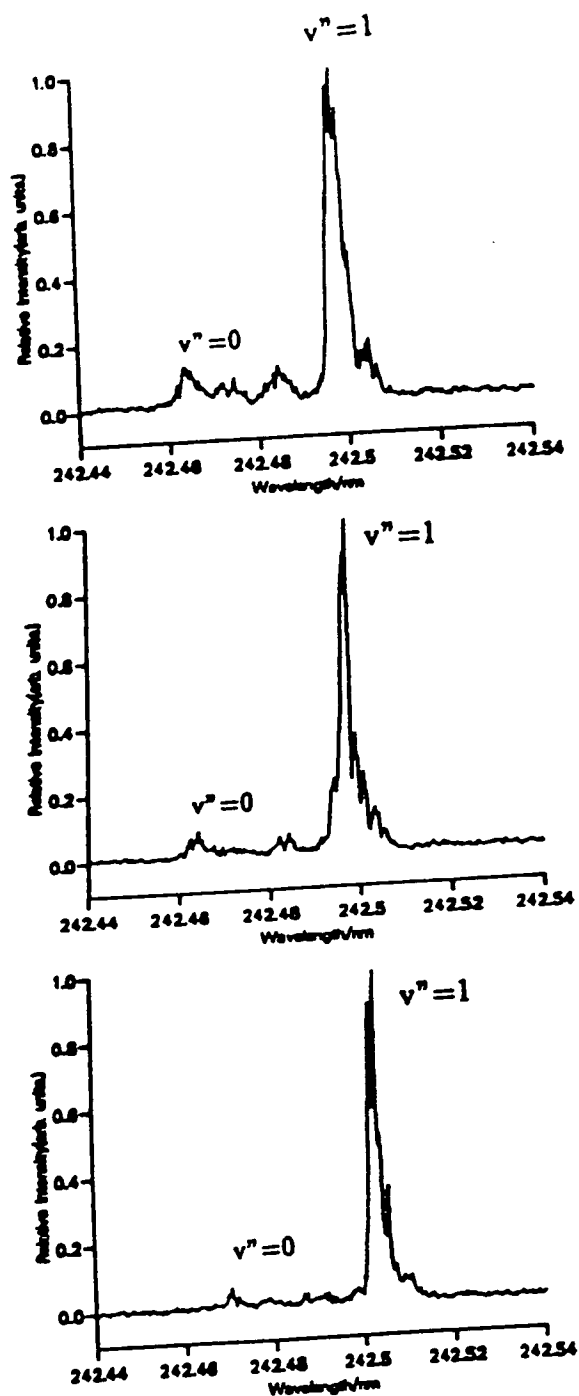


Figure 6-12: The sequence of spectra shown in this figure were recorded to demonstrate the effect on the $\text{HCl}(v''=1)$ signal of moving the outer injector closer to the laser focus. The top, middle and bottom spectra were obtained for laser-outer injector distances of 25 mm, 15 mm and 5 mm respectively. The inner injector was kept at a constant distance of 35 mm within the outer injector.

F(1-1) transition to the small neighbouring $v''=0$ peaks for the ‘best’ $v''=1$ production shown in figure 6-13, it possible to estimate the Q-head, F(0-0) to Q-head, F(1-1) ratio for this optimum $v''=1$ signal. It was found that the Q-head of the F(1-1) transition shown in figure 6-13 corresponds to an intensity approximately equal in size to the Q-head of the F(0-0) transition.

Having obtained a reliable source of $\text{HCl}(v'' = 1)$ it was intended to proceed to attempt to probe the vibrationally excited species via the B-X(11-1) transition. Unfortunately, at this point a major fault in our vacuum system developed, through the corrosion of the gate valve separating the reaction and detection chambers. Consequently, we never managed to carry out the original aims of this chapter, i.e. to map the (2+1) REMPI spectroscopy of the higher vibrational levels of the ground electronic state of HCl through the excited electronic $B^1\Sigma^+$ state. In the meantime to support potential future achievement of these aims, an alternative injector was constructed, which will hopefully increase the chance of seeing near nascent vibrational distributions. The previous concentric arrangement of injectors used before suffered from three main faults

- the gas density in the reaction region was not high enough to ensure frequent reactive collisions in a localised volume
- collisional relaxation of vibrationally excited products caused by the continuous flow of reagents into the reaction chamber
- damage to the vacuum system through pumping large quantities of corrosive gas.

Figure 6-14 shows a schematic of the newly constructed injector apparatus, which will hopefully alleviate the main problems discussed above. The outer injector is made of glass, with the bottom 5 cm coated with gold which allows it to be electrically floated so that it can be positioned in close proximity to the laser focus. The inner injector is a quartz discharge tube.

A larger (than in the previous design) instantaneous pressure is created in the reaction region by making the diameter of the exit channel from the injector to the vacuum chamber very small, in this case $140\mu\text{m}$ (measured with a microscope).

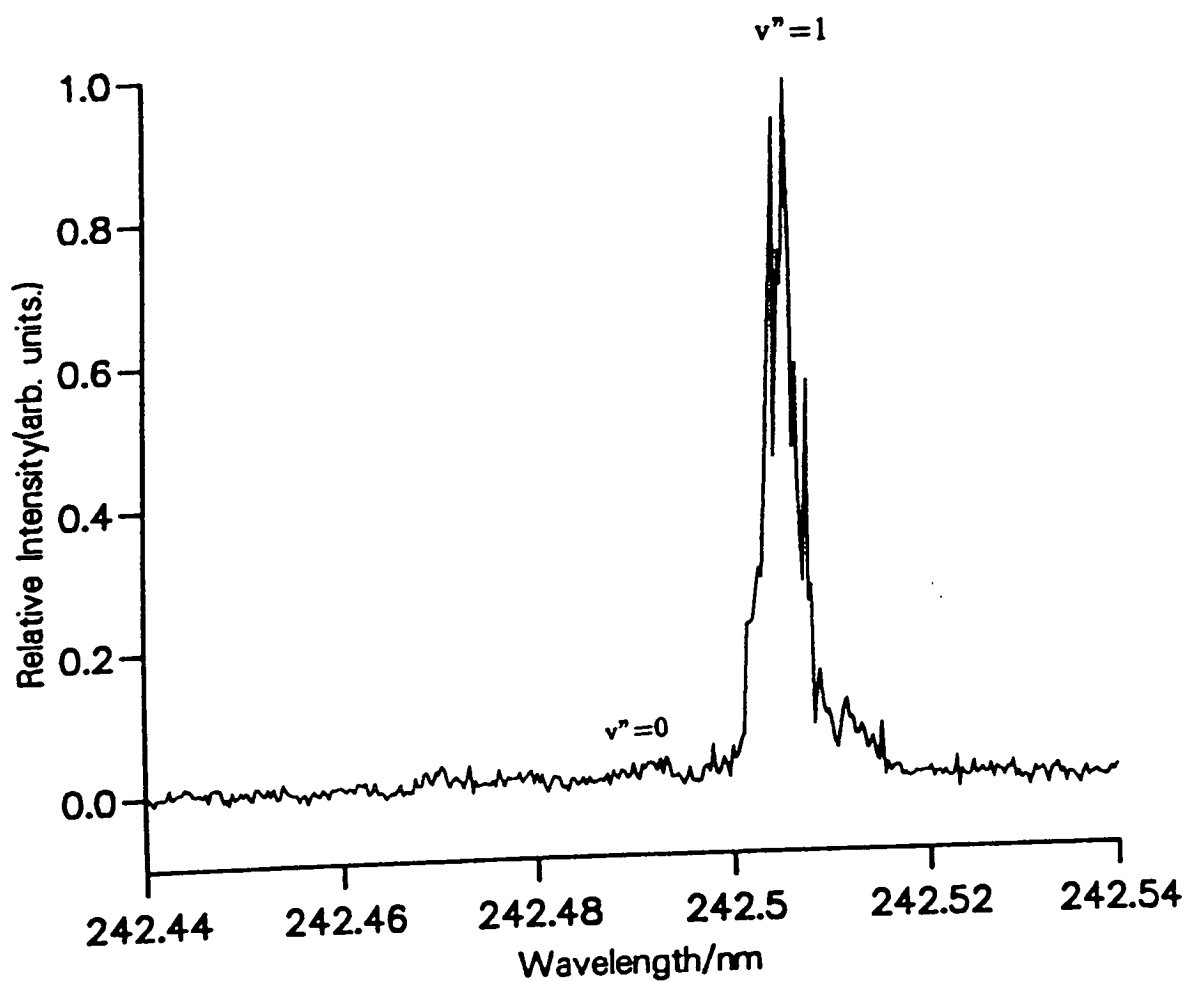


Figure 6-13: This figure shows the optimum production of $\text{HCl}(v''=1)$. It was obtained operating at a total pressure of 2 mTorr (1:1, $\text{Cl}_2:\text{H}_2$). The outer injector was 5 mm from the laser focus and the inner injector was 50 mm within the outer injector.

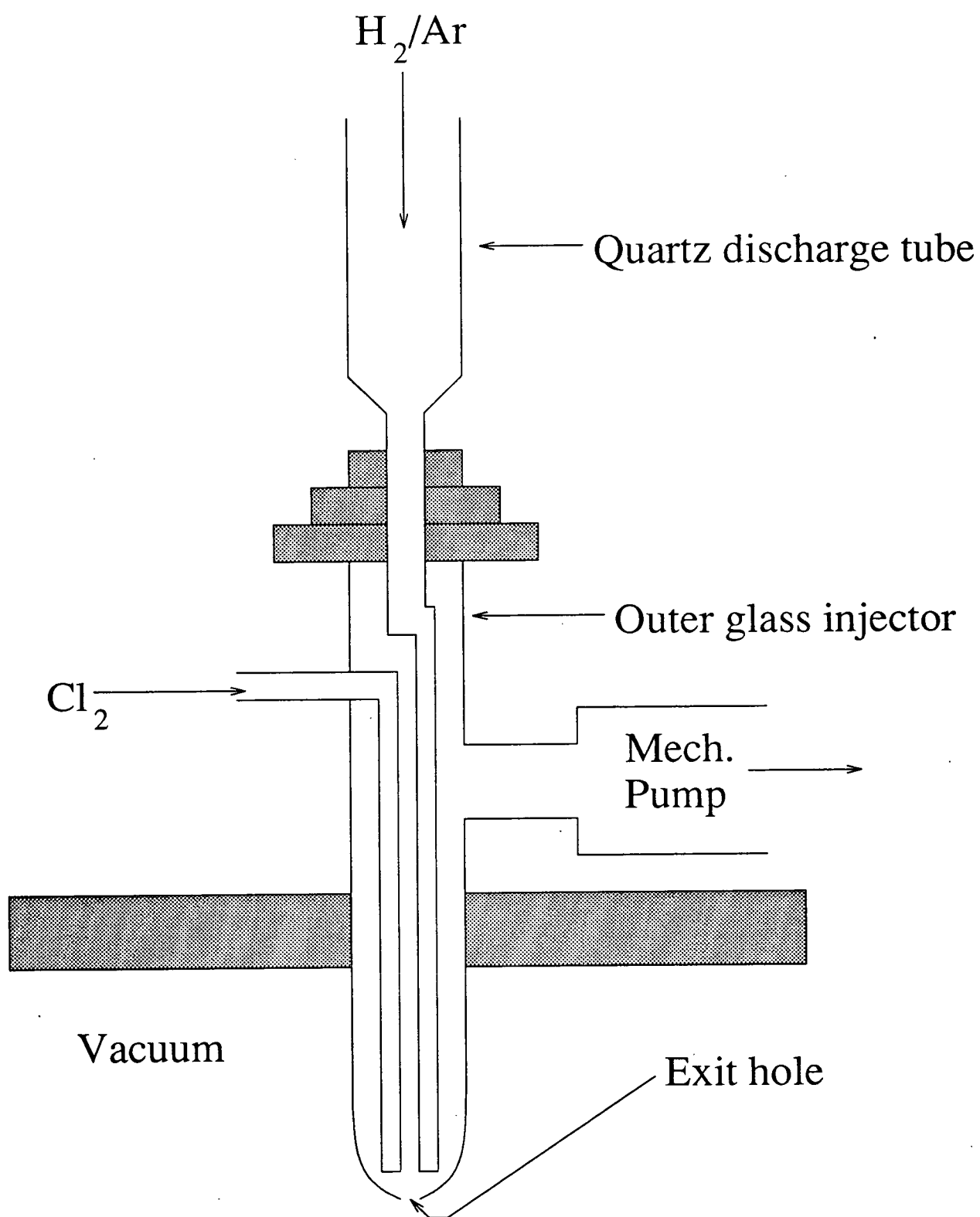


Figure 6-14: Schematic of the newly designed injector apparatus

Ortho-phosphoric acid was used to clean the injector, and kept the injector hole clear. The walls of the exit channel were made as thin as possible to reduce any deactivation of the products as they leave the injector and enter into the vacuum chamber.

From elementary gas kinetic theory[19] the mean free path, λ , is related to the pressure, P , via

$$\lambda = \frac{RT}{\sqrt{2}\pi d^2 N_a P} \quad (6.7)$$

where R is the gas constant, N_a is the Avogadro constant and d is the collision diameter of a molecule. With the previous injector apparatus, the maximum pressure allowed in the reaction region, without causing too high a pressure in the vacuum chamber, was 2 mTorr. A pressure of 2 mTorr of H_2 results in a mean free path of 0.04 m. The new injector apparatus permits a maximum pressure of 10 Torr in its reaction region, which results in a much shorter mean free path of $8\mu\text{m}$. Therefore, the new injector apparatus should substantially increase the number of reactive bimolecular collisions, leading to a higher density of vibrationally excited products. Collisional relaxation is reduced by continuously removing reagent gases from the reaction region by means of a high throughput rotary pump connected to the side arm of the injector. Corrosive gases are trapped in a liquid nitrogen cold trap, positioned before the rotary pump.

To test the feasibility of the new injector, some simple flow tests were carried out. When a gas at a temperature T , and a pressure P , is separated from a vacuum by a very small hole, area A_0 , the flow of gas through the hole per unit time is given by [19]

$$F = \frac{PA_0}{(2\pi mkT)^{1/2}} \quad (6.8)$$

where m is the mass of the particles flowing through the hole and k is the Boltzmann constant.

Therefore, by measuring the flow rate through the injector hole into the vacuum chamber for different backing pressures within the injector, it is possible to determine the predicted hole size. While this calculation is by no means intended to be an accurate measure of the hole size, it should confirm the proper functioning

of the injector. Flowing hydrogen through the injector for various backing pressures, gave a value of $130 \pm 5 \mu\text{m}$ for the hole diameter, which is in good enough agreement with the measured holesize. Unfortunately, the time before the repair of the gate valve precluded any attempt to verify the operation of the new injector with reactive gas flows.

6.5 Conclusions

The aim of this chapter was to establish the (2+1) REMPI spectroscopy of ground electronic state, rovibrationally excited HCl through the lower isolated and therefore unperturbed vibrational levels of the electronically excited $B^1\Sigma^+$ state.

Although this aim has not been completely realised (due to a fault in the vacuum apparatus) significant achievements have been made towards it

- the most favourable bands to probe the vibrationally excited products have been potentially identified through calculating the Franck-Condon factors between the $B^1\Sigma^+$ and $X^1\Sigma^+$ states
- a method has been developed which allows the optimum production of $\text{HCl}(v'' = 1)$ through the $\text{H} + \text{Cl}_2 \longrightarrow \text{HCl}^\dagger + \text{Cl}$ reaction and detection via the (2+1) REMPI $F^1\Delta(2) \longleftarrow X^1\Sigma^+(1-1)$ transition.

Future experiments will continue to attempt to achieve the above aim and, in particular, to locate the lower isolated and therefore unperturbed vibrational levels of the electronically excited $B^1\Sigma^+$ state. Once a reliable source of $\text{HCl}(v'' = 1)$ is re-established the B-X(11-1) transition will be recorded. Attempts to map the (2+1) REMPI spectroscopy of the higher vibrational levels will be attempted using the new injector apparatus since relaxation of the higher vibrational levels is anticipated to be less with this injector.

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Chapter 7

Jet Cooled Spectroscopy of HCl

7.1 Introduction

The ultimate aim of this thesis was to carry out hot atom dynamics experiments of the type described in chapter 1. The typically low densities of product molecules formed in such experiments requires high sensitivity detection methods. LIF detection of nascent products is facilitated by operating at total reactant pressures of typically $\sim 1 \times 10^{-4}$ mbar, which gives rise to reasonable product densities and hence reasonable fluorescence signals. However, pressure constraints in mass-resolved REMPI experiments are far stricter, since the microchannel plate detector can only operate at pressures of $\leq 1 \times 10^{-6}$ mbar. Our vacuum apparatus can permit a maximum pressure of 3.5×10^{-4} mbar in the reaction chamber, whilst maintaining a pressure of 1×10^{-6} mbar in the detection chamber. To achieve such a pressure differential the top hat flange, separating the reaction and detection chambers, could be fitted with a conductively coated capillary array (see subsection 2.2.1). The lower ion transmission through the capillary array may compromise any original gain achieved by increasing the gas density within the source region. Therefore, it is unlikely that a massive gain in the ratio of product signal to noise would be achieved. Operating at higher total pressures within the reaction chamber may also introduce the possibility of space charging of the photoions from non-resonantly ionised species.

From an entirely practical point of view it is damaging (and expensive) to continually pump large amounts of corrosive gas through the vacuum system.

All of the above arguments encouraged us to purchase a General Valve Corporation pulsed molecular beam valve for admitting gases into the vacuum system.

Pulsed molecular beam valves are capable of producing directional, high density pulses of gas which may have a density of 100-1000 times that of an effusive source[1]. However, the total gas load admitted into the vacuum chamber is low, which means small amounts of gas are used and corrosion is kept low. The main requirement for using molecular beam valves is that there is enough pumping capacity to cope with the high density gas pulses.

As well as increasing the number density gain the use of molecular beam valves also allows jet-cooling of the reagents. This introduces certain advantages in a hot atom dynamics type experiment. The ability to vary the *average* collision energy by changing the photolysis wavelength is a potential virtue of a hot atom dynamics experiment. Equation (A.6) in appendix A gives an analytical expression for the distribution of collision speeds resulting from precursor and reactant thermal motions in a hot atom dynamics experiment. From this expression the collision energy can be seen to scale with the square root of the temperature. Therefore, for most reactions at ambient temperatures the resultant distribution limits the ability of investigating how the collision energy can affect a reaction, particularly the details of the variation of the cross section with collision energy. Jet-cooling of the reagents can substantially reduce the collision energy spread, for example lowering the temperature from 300 K to 5 K reduces the collision energy spread by almost a factor of 8. The other significant advantage obtained via jet-cooling is that reagents can be prepared in a single rovibrational state which enables quantum state reaction cross sections to be evaluated. This has recently been applied by Whitaker *et al*[3] in an investigation into the rotational energy transfer for collisions between Ar and NO($^2\Pi_{1/2}$, $v=0$, $J=0$).

To ensure that the molecular beam valve was performing as it is expected to, we decided to try and obtain some (2+1) REMPI jet cooled spectra of HCl.

7.2 Supersonic Molecular Beams

The flow of gas from a high pressure reservoir through a small hole into a vacuum chamber creates a molecular beam. This flow is characterised by two parameters, namely the mean free path of the source gas, λ_0 , and the dimension of the source orifice which limits the flow, D . The relative size of these parameters determines the behaviour of the molecular beam emerging from the source orifice into the vacuum chamber.

In an effusive molecular beam, λ_0 is of the order of or is larger than D . Gas molecules leave the source largely unperturbed by collisions with one another, so that the beam produced has the same bulk properties as the source gas.

In contrast, if λ_0 is small compared to D , then the density of the source gas is high close to the aperture and the molecules undergo many collisions with one another as they flow through the orifice. It is possible to treat the gas as a continuous fluid, according to the laws of hydrodynamic flow. The fluid requires a net velocity in response to a pressure gradient across the nozzle. This type of flow occurs in supersonic nozzle sources. If there is a collimating aperture downstream of the source, such as a skimmer, the resulting expansion is known as a supersonic molecular beam. If this aperture is absent, the resulting flow of gas is known as a supersonic free jet.

Since the divergence of a supersonic beam or jet is less than that of an effusive beam, the relative flux through a given area perpendicular to the direction of flow is higher for a supersonic source. The increase in forward velocity of the beam comes from a reduction in the local enthalpy of the gas. The lowering in temperature, from T_i to T_f , accompanying the expansion is given by the well known expression[2]

$$\frac{T_f}{T_i} = \left[1 + \frac{\gamma - 1}{2} M^2 \right]^{-1} \quad (7.1)$$

where γ = the ratio of the specific heats of the gas at constant pressure and volume = C_P/C_V and M is the Mach number (the ratio of the stream velocity to the local speed of sound).

For a monoatomic gas[2]

$$M = 3.26(x/D - 0.075)^{0.67} - 0.61(x/D - 0.075)^{-0.67} \quad (7.2)$$

and for a diatomic gas[2]

$$M = 3.65(x/D - 0.4)^{0.4} - 0.82(x/D - 0.4)^{-0.4} \quad (7.3)$$

Plots of M versus x/D and T_f/T_i versus M are shown in figures (7-1) and (7-2) respectively.

Figure (7-1) suggests that we might expect to produce a beam of any desired Mach number. However, there comes a point in the beam where the collision rate becomes so low that free molecular flow occurs and no further expansion takes place. This point defines the terminal Mach number which is defined as

$$M_T = 1.2 \left[\frac{\lambda_0}{D} \right]^{-0.4} \quad (7.4)$$

A second complication arises from the presence of shock waves in the expanding jet. Particularly important is the shock front perpendicular to the flow direction known as the Mach disc. This shock is believed to originate in collisions of the beam molecules with the background gas. The distance of this disc, x_M , from a nozzle of diameter D varies roughly as

$$\frac{x_M}{D} = 0.67 [P_0/P]^{1/2} \quad (7.5)$$

where P_0 is the reservoir pressure and P is the pressure in the expansion chamber.

In a beam of molecules having internal energy, some of the energy for the increase in forward translational energy can come from vibration or rotation. The main reason for the wide use of supersonic molecular beams in spectroscopy is due to the fact that the rotational and vibrational degrees of freedom can reach equilibrium with the cold translational bath. The rotational and vibrational degrees of freedom of polyatomic molecules are relaxed by collisions as the translational temperature decreases, but the rate of cooling lags behind that of a monoatomic gas under similar conditions. Maximum cooling of polyatomic molecules is achieved by seeding a small amount of the polyatomic into an expansion of a monoatomic gas such as He or Ar. The properties of the expansion are approximately those of the weighted average of the mixture of the two species.

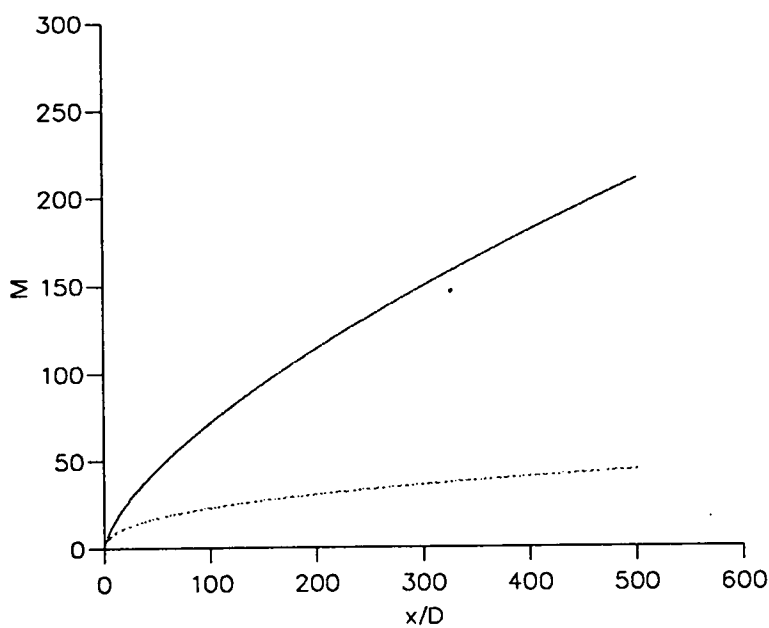


Figure 7-1: The Mach number as a function of the dimensionless parameter, x/D , for a monoatomic gas (solid line) and for a diatomic gas (dotted line).

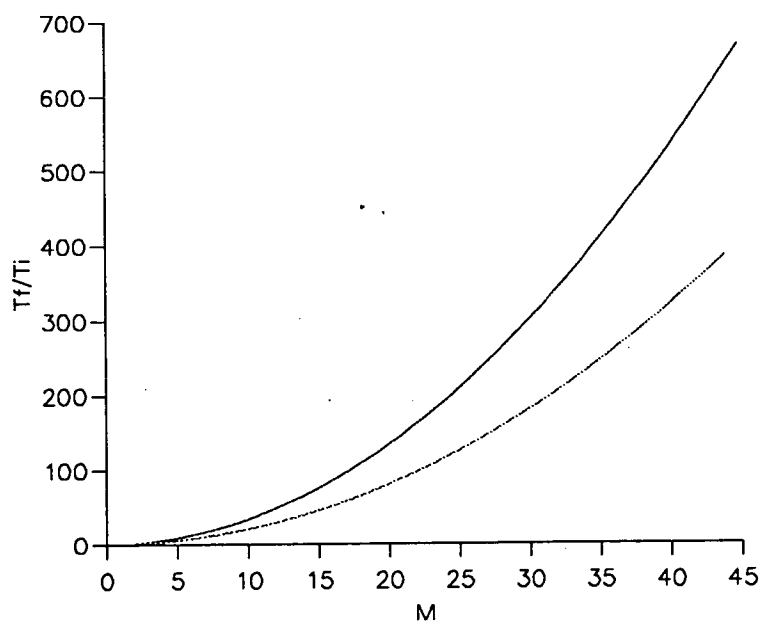


Figure 7-2: The reduced temperature ratio as a function of Mach number for a monoatomic gas (solid line) and for a diatomic gas (dashed line).

Rotational relaxation by collisions is a fairly efficient process, so that the rotational temperature of the molecules in a supersonic expansion follows the translational temperature reasonably closely. In general, collisional vibrational relaxation is a less efficient process, and the vibrational temperature lags behind both the translational and rotational temperatures.

7.3 Experimental

The apparatus used to carry out jet cooled (2+1) REMPI of HCl was essentially the same as that described in section (5.4.1), except that gas was introduced into the reaction chamber via a molecular beam valve (see section 2.4.2).

The expansion conditions were probed by monitoring the REMPI signal of HCl in ($v'' = 0$) as a function of the delay between the ionising laser and the pulsed valve. The digital pulse delay generator (see subsection 2.6.5) was used to synchronise the laser, pulsed valve sequence and TOF ion signal processing. These measurements provided direct information on the length of the molecular beam pulse. Care was taken that the experiments were performed when the valve was fully opened. This could easily be observed by changing the length of the pulse in the pulsed valve's power supply and observing that the amplitude of the signal was constant and that only the length varied.

The laser beam focus was positioned about 4 cm beneath the centre of the valve orifice and crossed the gas jet perpendicular to the flow axis (see figure 2-6).

Various seeding ratios of ~~HCl~~ (99.9% purity, Matheson) in Ar (BOC, 99.998% purity) were expanded through the valve over a range of backing pressures. Two valve orifice diameters were used, 500 μm and 150 μm . Careful control of the total HCl density eliminated any space charging of ion signals. Ion signals were collected for the parent molecular ion only (H^{35}Cl^+) and were typically averaged over 16 laser shots.

7.4 Results and Discussion

These preliminary experiments were carried out over the F(0-0) transition. Figure (7-3) shows the O-, P-, Q-, R- and S-branches of a room temperature spectrum of the F(0-0) transition. This figure has already been shown (figure 5-14), but is shown again for comparison with the first jet-cooled spectrum shown in figure (7-4). This spectrum was obtained using a 10% HCl in Ar mixture, operating at a backing pressure of 0.6 Atm, behind a 500 μ m diameter valve orifice. It shows the marked decrease in the intensity of the P- and Q-branches relative to the R-branch. This reflects the fact that the first Q- and P-lines originate from $J'' = 2$ and $J'' = 3$, respectively, whereas the first R-line occurs from $J'' = 1$ i.e. there has been a shift in the ground state rotational populations towards the lower J'' rotational levels. The evidence for cooling is further substantiated by the noticeable reduction in intensity of the higher J'' rotational levels of the P- and R-branches, compared to the room temperature spectrum.

The spectrum shown in figure (7-4) was recorded under fairly mild conditions. Figure (7-5) shows a much colder spectrum obtained operating at a higher backing pressure of 2.5 Atm with a decreased seeding ratio of 1% HCl to 99% Ar.

Backing pressures of more than 2.5 Atm for this particular valve orifice size could not be tolerated due to the limited pumping speed of our vacuum system. However, higher backing pressures were made possible by changing to a 150 μ m valve orifice. Figure (7-6) shows the spectrum obtained operating at much more extreme valve conditions using a 0.5% HCl in Ar mixture at a backing pressure of 5.6 Atm behind a 150 μ m diameter valve orifice. Only S(0) and R(1) are clearly visible in this spectrum, implying that most of the ground state population is in the $J'' = 0$ and $J'' = 1$ rotational levels. R(2) and S(0) are separated by 0.7 cm^{-1} and are not resolvable within the bandwidth of our laser. However, the contribution from R(2) to the R(2)/S(0) intensity is likely to be negligible since the Q(2) line (which has a rotational linestrength value almost identical to that for R(2)) is absent from the spectrum shown in figure (7-6). A simulated spectrum with a rotational temperature of 10 K is shown in figure (7-7). While no attempt

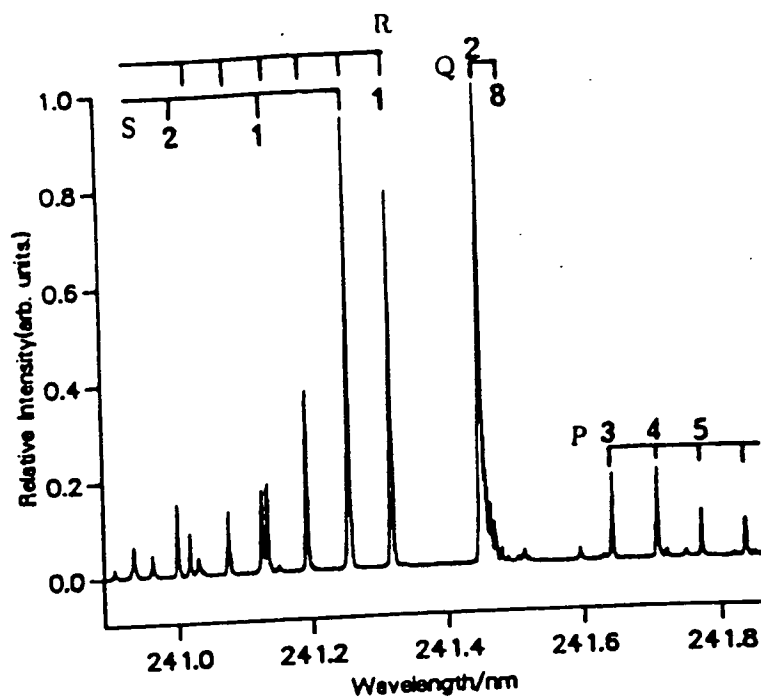


Figure 7-3: (2+1) REMPI spectrum of HCl taken at room temperature, showing the O,P,Q,R and S-branches of the F(0-0) transition.

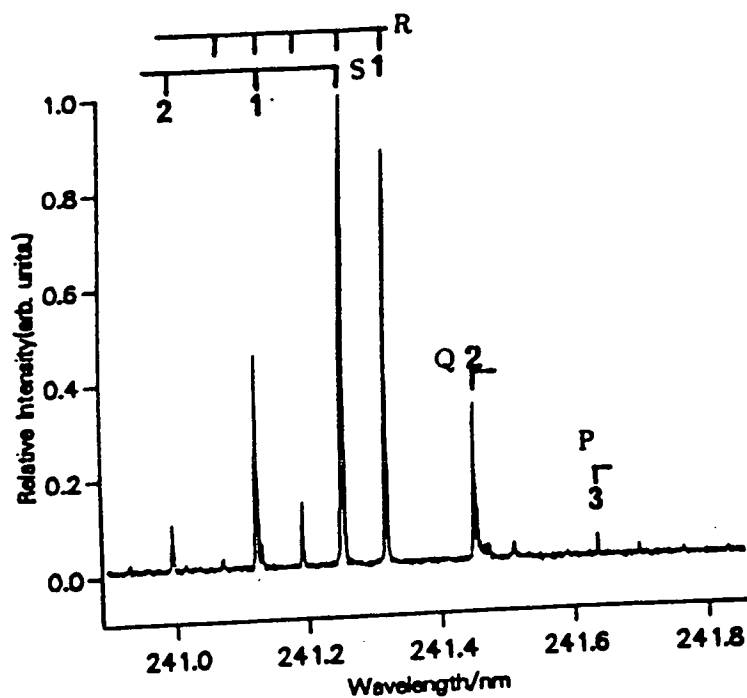


Figure 7-4: (2+1) REMPI spectrum of HCl showing the first signs of jet cooling. The spectrum was obtained using a 10% HCl in Ar mixture, operating at a backing pressure of 0.6 Atm, behind a 500 μ m diameter orifice.

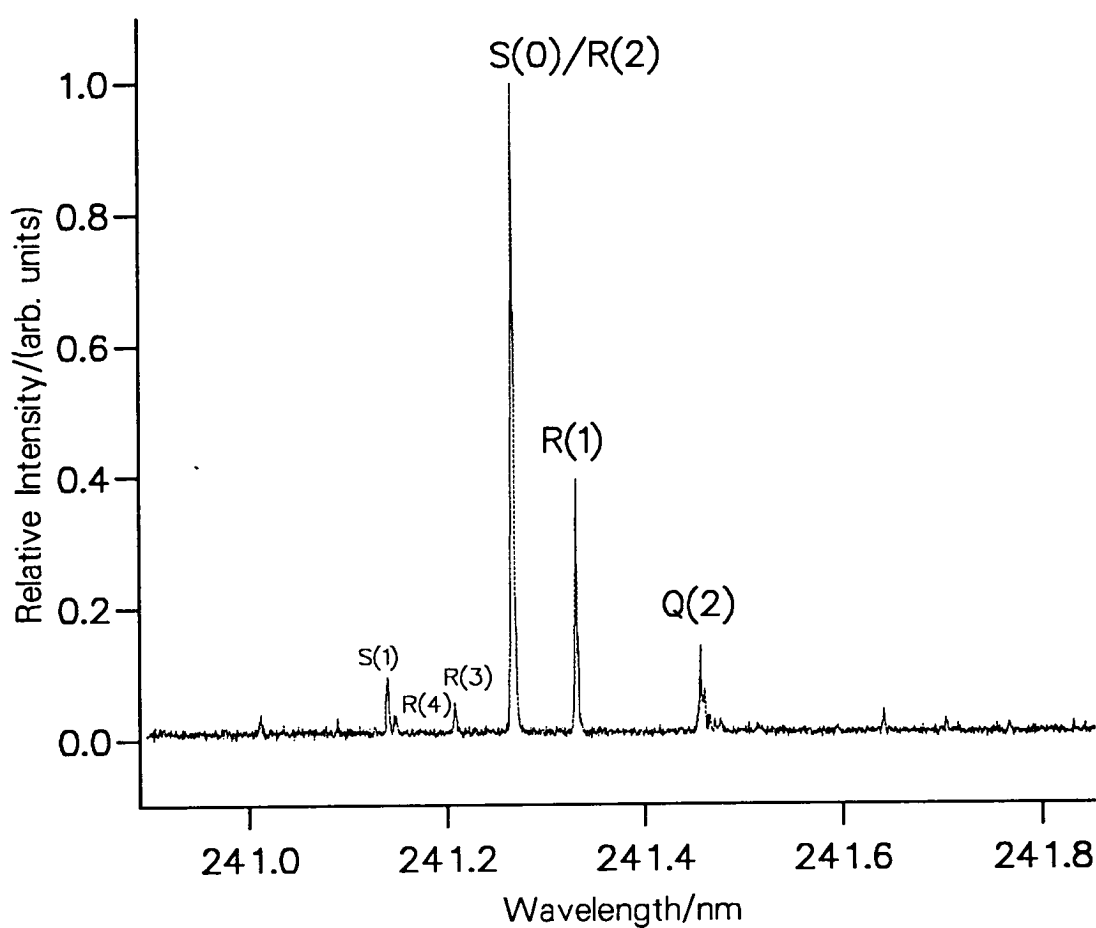


Figure 7-5: (2+1) REMPI spectrum of HCl, showing the improved jet-cooling obtained using a 1% HCl in Ar mixture, operating at a backing pressure of 2.5 Atm behind a 500 μ m diameter valve orifice.

was made to accurately calculate the rotational temperature produced in figure (7-6), the similarity between the experimental and simulated spectra indicate that a rotational temperature of approximately 10 K was achieved.

The degree of cooling also varies through the gas pulse. This is shown in figure 7-8, which shows three spectra which were recorded simultaneously, under the same experimental conditions, for three different time delay settings between the valve opening and the laser firing. The presence of higher rotational lines and a decrease of the S(0)/R(1) ratio at longer times into the gas pulse indicates a warming effect. This can perhaps be attributed to collisions between background scattered gas (from the front edge of the gas pulse) and the tail end of the gas pulse. The calculated position of the Mach disc, under the various valve conditions, made it unfeasible that the warming effect was due to collisions between the jet and the ambient background gas.

In conclusion, through the study of the (2+1) REMPI spectroscopy of jet cooled HCl, we have demonstrated the successful implementation of a pulsed molecular beam valve into our apparatus. This has provided an extremely substantial increase in the instantaneous number density which can be accommodated in the reaction zone, without overloading the systems pumping capacity or resulting in an unacceptably high pressure at the microchannel plate detector. An estimated gain of $\sim 10^3$ has been achieved in the detection sensitivity using a molecular beam valve source compared to a simple effusive source. This estimate was made by comparing (2+1) REMPI HCl signals recorded under similar conditions, (pressure in the reaction chamber, probe laser power, detector setting etc.), for effusive and molecular beam sources. Future hot atom dynamics experiments, incorporating REMPI-TOF detection, should therefore stand a higher chance of success.

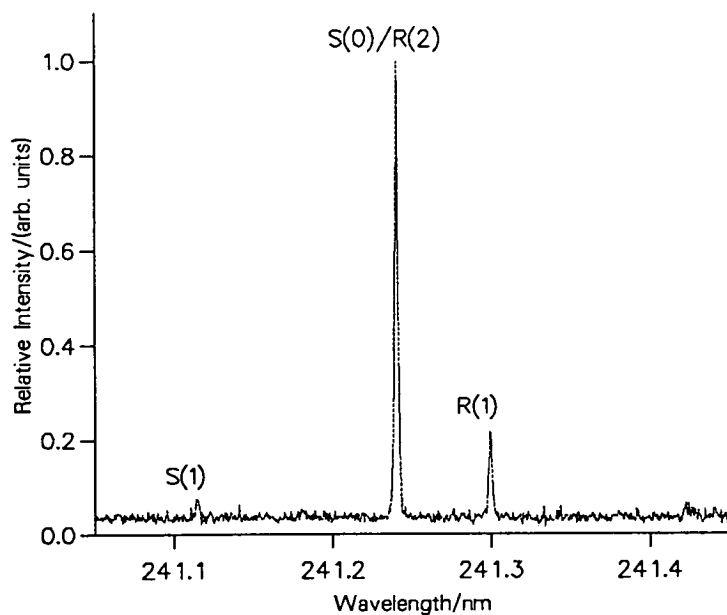


Figure 7-6: (2+1) REMPI spectrum of HCl showing the most rotationally cooled spectrum obtained over the F(0-0) region. The spectrum was obtained using a 0.5% HCl in Ar mixture, operating at a backing pressure of 5.6 Atm behind a 150 μ m diameter valve orifice.

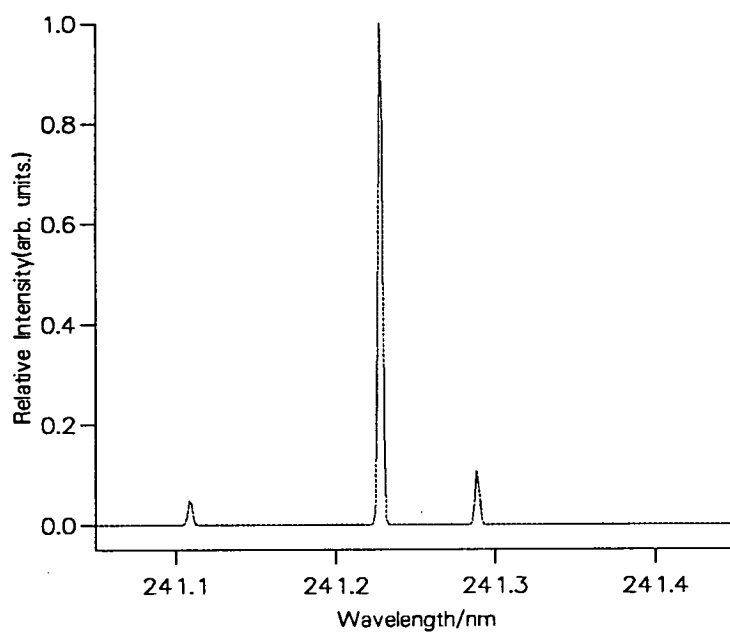


Figure 7-7: Simulation of the (2+1) REMPI for HCl over the same wavelength region as the spectrum above, for a rotational temperature of 10 K.

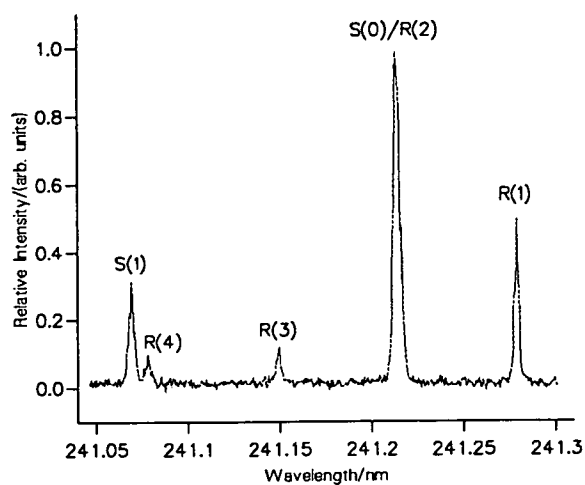
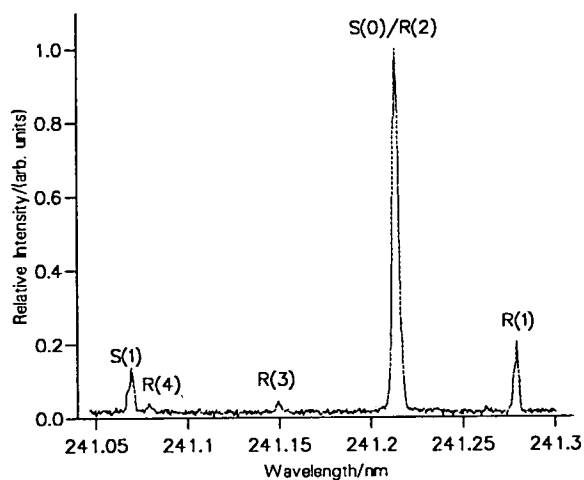
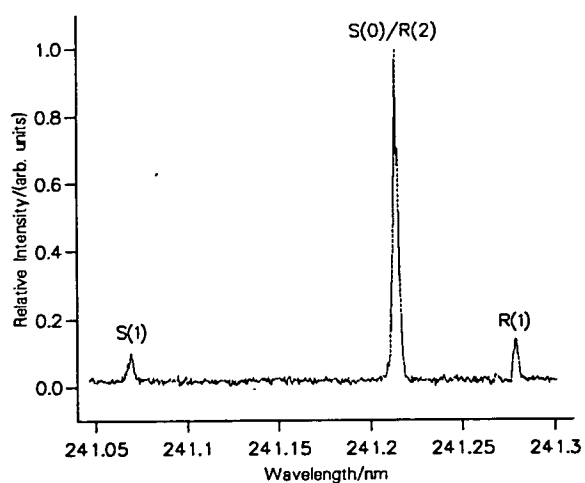


Figure 7–8: The spectra shown in this figure were recorded simultaneously under the same experimental conditions, for 3 different time delay settings between the valve opening and the laser firing. The time delays were; 410 μ s (top spectrum), 460 μ s (middle spectrum) and 560 μ s (bottom spectrum).

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Appendix A

Velocity Averaging Effects in Hot Atom Reaction Dynamics

In this appendix analytical expressions are derived which quantify the effects of velocity averaging in hot atom polarisation experiments. The derivations are summarised versions of work presented in reference [1].

It is very well known[2] that the centre-of-mass angular distribution of recoil velocities, $\mathbf{u}_A$, of a fragment produced by linearly polarised photolysis is given by

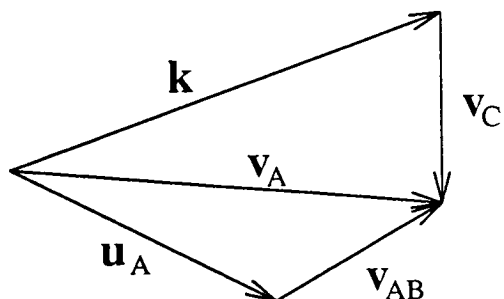
$$w(\hat{\mathbf{E}}, \mathbf{u}_A) d\Omega = \frac{1}{4\pi} \{1 + \beta P_2(\hat{\mathbf{E}} \cdot \hat{\mathbf{u}}_A)\} d\Omega \quad (\text{A.1})$$

where $\hat{\mathbf{E}}$ and $\hat{\mathbf{u}}_A$ are unit vectors in the direction of linear polarisation and the recoil direction, respectively. P_2 is the second order Legendre polynomial. The solid angle, Ω , is defined by $d\Omega = d(\hat{\mathbf{E}} \cdot \hat{\mathbf{u}}_A) d\phi = \sin\theta d\theta d\phi$, where θ is the angle between $\hat{\mathbf{E}}$ and $\mathbf{u}_A$, and ϕ is a cylindrically symmetric azimuthal angle. The anisotropy parameter, β , defines the shape of the distribution. It is related to the correlation between $\mathbf{u}_A$ and the transition dipole moment vector $\hat{\mu}$, and hence to $\hat{\mathbf{E}}$, by

$$\beta = 2 \langle P_2(\hat{\mu} \cdot \hat{\mathbf{u}}_A) \rangle = 5 \langle P_2(\hat{\mathbf{E}} \cdot \hat{\mathbf{u}}_A) \rangle \quad (\text{A.2})$$

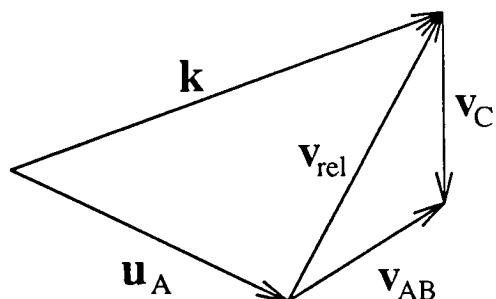
(where the angled brackets $\langle \rangle$ imply an expectation value averaged over all values).

A natural way to proceed with the calculation of the final laboratory frame distribution, $w(\hat{\mathbf{E}}, \mathbf{k})$, of A...C collision velocity vectors, $\mathbf{k}$, is to follow essentially the logical sequence of the steps in the experiment, as illustrated in figure A-1(a).



$$(a) \quad \mathbf{v}_A = \mathbf{u}_A + \mathbf{v}_{AB} ;$$

$$\mathbf{k} = \mathbf{v}_A + \mathbf{v}_C$$



$$(b) \quad \mathbf{v}_{rel} = \mathbf{v}_{AB} + \mathbf{v}_C ;$$

$$\mathbf{k} = \mathbf{u}_A + \mathbf{v}_{rel}$$

Figure A-1: Alternative sequences of combining vector distributions to produce the laboratory frame distribution of collision velocity vectors.

The effect of the thermal distribution of precursor velocities, $\mathbf{v}_{AB}$, on laboratory-frame fragment recoil velocities, $\mathbf{v}_A$, is first obtained for a fixed centre-of-mass recoil velocity, $\mathbf{u}_A$, by integration over all magnitudes and directions of $\mathbf{v}_{AB}$. The actual distribution of laboratory - frame recoil velocities, $w(\hat{\mathbf{E}}, \mathbf{v}_A)$, from polarised laser photolysis is then obtained by integration over all directions (the speed u_A is assumed fixed) distributed according to $w(\hat{\mathbf{E}}, \mathbf{k})$ in equation A-1.

A very similar calculation to that of the effect of $\mathbf{v}_{AB}$ on $\mathbf{v}_A$ for a fixed $\mathbf{u}_A$ will reveal the effect of the thermal distribution of $\mathbf{v}_C$ on the distribution of $\mathbf{k}$ for a fixed value of $\mathbf{v}_A$. Integration of this result over the distribution, $w(\hat{\mathbf{E}}, \mathbf{k})$, for the distribution of $\mathbf{k}$ about $\hat{\mathbf{E}}$.

Proceeding mathematically, the Maxwell-Boltzmann distribution of $\mathbf{v}_{AB}$ is simply

$$f(\mathbf{v}_{AB})d\mathbf{v}_{AB} = \left(\frac{m_{AB}}{2\pi k_B T}\right)^{3/2} \times \exp\left(\frac{-m_{AB}\mathbf{v}_{AB}^2}{2k_B T}\right)d\mathbf{v}_{AB} \quad (\text{A.3})$$

where m_{AB} is the mass of AB, k_B is the Boltzmann constant and T is the common temperature of the system. The effect which this has on the distribution of $\mathbf{v}_A$ for a fixed $\mathbf{u}_A$ results in a shifted Maxwell-Boltzmann distribution,

$$f(\mathbf{v}_A, u_A)d\mathbf{v}_A = \left(\frac{m_{AB}}{2\pi k_B T}\right)^{3/2} \times \exp\left\{\frac{-m_{AB}(\mathbf{v}_A - \mathbf{u}_A)^2}{2k_B T}\right\} d\mathbf{v}_A \quad (\text{A.4})$$

which depends parametrically on u_A .

The integration of this expression over the photolytic angular distribution in equation A-1 has also been tackled previously [3][4]. The essential feature of the result is that it is expressible as a modified version of equation A-1 in which the magnitude and angular variables are no longer separable, with a speed-dependent shape parameter, $\beta_{eff}(v_A)$; i.e.

$$w(\hat{\mathbf{E}}, \mathbf{v}_A)dv_A d(\hat{\mathbf{E}} \cdot \hat{\mathbf{v}}_A) = A(v_A) \left\{1 + \beta_{eff}(v_A)P_2(\hat{\mathbf{E}} \cdot \hat{\mathbf{v}}_A)\right\} dv_A d(\hat{\mathbf{E}} \cdot \hat{\mathbf{v}}_A) \quad (\text{A.5})$$

where we have carefully resolved the angular and magnitude variables: this expression is no longer differential in a cylindrically symmetric azimuthal angle over which it has already been integrated, and is normalised when integrated over all directions and magnitudes of v_A . The quantities $A(v_A)$ and $\beta_{eff}(v_A)$ are both parametrically dependent on u_A , and are related to velocity-dependent Legendre

moments (averaged over angular coordinates only). The premultiplier $A(v_A)$ is the collision speed distribution[5];

$$A(v_A) = (1/2) < P_0(\hat{\mathbf{E}} \cdot \hat{\mathbf{v}}_A) > \quad (\text{A.6})$$

$$= (v_A/u_A) \left(\frac{1}{2\pi\nu^2} \right)^{1/2} \times \exp \left\{ \frac{-(u_A^2 + v_A^2)}{2\nu^2} \right\} \sinh \left(\frac{u_A v_A}{\nu^2} \right) \quad (\text{A.7})$$

$$= \left(\frac{1}{2\nu^2} \right) \left(\frac{v_A^3}{u_A} \right)^{1/2} \times \exp \left\{ \frac{-(u_A^2 + v_A^2)}{2\nu^2} \right\} I_{1/2} \left(\frac{u_A v_A}{\nu^2} \right) \quad (\text{A.8})$$

whereas $\beta_{eff}(v_A)$ is proportional to the second Legendre moment, normalised to the speed distribution;

$$\beta_{eff}(v_A) = 5 < P_2(\hat{\mathbf{E}} \cdot \hat{\mathbf{v}}_A) > / < P_0(\hat{\mathbf{E}} \cdot \hat{\mathbf{v}}_A) > \quad (\text{A.9})$$

$$= \beta \left\{ 1 + 3 \left(\frac{\nu^2}{u_A v_A} \right)^2 - \left(\frac{3\nu^2}{u_A v_A} \right) \frac{\cosh(u_A v_A / \nu^2)}{\sinh(u_A v_A / \nu^2)} \right\} \quad (\text{A.10})$$

$$= \beta \frac{I_{5/2}(u_A v_A / \nu^2)}{I_{1/2}(u_A v_A / \nu^2)} \quad (\text{A.11})$$

In equations A-7 to A-11 the parameter ν is defined by

$$\nu = \left(\frac{k_B T}{m_{AB}} \right)^{1/2} \quad (\text{A.12})$$

and is a measure of the thermal velocity of the precursor, AB. The terms $I_{n+1/2}$ denote modified spherical Bessel functions, introduced previously in the solution to problems of this type (for example[3]). Equation A10 has the expected form of a product of an independent β factor from photolysis and a broadening factor due to the thermal motion.

The proof was initially completed by integrating the analogue of equation A-4, describing the effect of $\mathbf{v}_C$ on the collision velocity for fixed $\mathbf{v}_A$, over all directions and magnitudes of $\mathbf{v}_A$ described by equation A-5. This is a substantially more algebraically arduous calculation than any of the others above, because of the dependence of β_{eff} on the speed, v_A : the details are not presented here. However, the final result can be cast into the familiar form

$$w(\hat{\mathbf{E}}, \mathbf{k}) d\mathbf{k} d(\hat{\mathbf{E}} \cdot \hat{\mathbf{k}}) = A(k) \left\{ 1 + \beta_{eff}(k) P_2(\hat{\mathbf{E}} \cdot \hat{\mathbf{k}}) \right\} d\mathbf{k} d(\hat{\mathbf{E}} \cdot \hat{\mathbf{k}}) \quad (\text{A.13})$$

with exactly analogous expressions to those in equations A-5 to A-12 describing the various terms, except with $\mathbf{k}$ replacing $\mathbf{v}_A$, k replacing v_A , and ω replacing ν , respectively throughout, where

$$\omega = \left\{ \frac{k_B T (m_{AB} + m_C)}{m_{AB} m_C} \right\}^{1/2} \quad (\text{A.14})$$

The last result is perhaps the key to understanding why equation A-13 is identical in form to equation A-5, and suggests a much more efficient route to its solution. The mass parameter in equation A-14 is simply the reduced mass of a "virtual collision" between the precursor and target molecules. The physical reason for its appearance is that the pair of velocities $\mathbf{v}_{AB}$ and $\mathbf{v}_C$ which separately affect the ultimate collision velocity, $\mathbf{k}$, are chosen randomly from two isotropic Maxwell-Boltzmann distributions. The net effect therefore depends on the relative velocity of AB and C, $\mathbf{v}_{rel}$, which is itself very well known to be an isotropic distribution, analogous to equation A-3, dependent on the common temperature and appropriate reduced mass. Correspondingly, equation A-13 can be deduced with much less intermediate algebra by combining the vector distributions in the order shown in figure A-1(b), and integrating the speed-independent angular distribution from photolysis over a single isotropic Maxwell-Boltzmann distribution.

Although the precise details of the distribution of $\mathbf{k}$ will be required in some cases, it will often be sufficient to assess its overall degree of anisotropy, averaged over all speeds k . The required "doubly averaged" second Legendre moment, $\langle\langle P_2(\hat{\mathbf{E}} \cdot \hat{\mathbf{k}}) \rangle\rangle$, is obtained by rearranging the analogue of equation A-9, implied by equation A-13, to solve for the "singly averaged" second moment $\langle P_2(\hat{\mathbf{E}} \cdot \hat{\mathbf{k}}) \rangle$ in terms of $\beta_{eff}(k)$ analogous to equation A-10 or A-11. The expression is then explicitly integrated over all values of k , yielding a result which may be written

$$\langle\langle P_2(\hat{\mathbf{E}} \cdot \hat{\mathbf{k}}) \rangle\rangle = (1/5)\beta \left\{ 1 - 3\left(\frac{\omega}{u_A}\right)^2 + 3\sqrt{2}\left(\frac{\omega}{u_A}\right)^3 F\left[\left(\frac{u_A^2}{2\omega^2}\right)^{1/2}\right] \right\} \quad (\text{A.15})$$

where $F(y)$ is the tabulated[6] Dawson's integral defined by

$$F(y) = \exp(-y^2) \int_0^y \exp(r^2) dr \quad (\text{A.16})$$

In fact, in many collisional experiments the signal which is measured is proportional to the rate of collisions, whereas all the expressions above describe the relative probabilities of finding pairs of A and C particles moving with a given relative collision velocity. The rate of collisions is weighted by a further factor of k , in addition to dimensional quantities related to the cross section for the process, pressures of reagents, efficiency of photolysis, etc.

It is possible to define a “normalised” rate of collisions with laboratory frame velocity $\mathbf{k}$ as

$$z(\hat{\mathbf{E}}, \mathbf{k}) d\mathbf{k} d(\hat{\mathbf{E}} \cdot \mathbf{k}) = C w(\hat{\mathbf{E}}, \mathbf{k}) k d\mathbf{k} d(\hat{\mathbf{E}} \cdot \hat{\mathbf{k}}) \quad (\text{A.17})$$

where the choice of constant, C , to satisfy the normalisation condition of an integral over all speeds and directions depends on the units adopted for the collision rate. Regardless of the value of C , the speed-dependent angular properties of the rate of collisions are exactly the same as those of the collision pairs: in an equation of the form of equation A-5, only the leading $A(k)$ term is altered, with $\beta_{eff}(k)$ unchanged.

However the weighting of contributing speeds is obviously altered, which therefore affects the result for the doubly averaged second Legendre moment integrated over all speeds (although the specific value of C remains irrelevant). The following expression was obtained

$$\langle\langle P_2(\mathbf{E} \cdot \mathbf{k}) \rangle\rangle_z = (1/5)\beta \left\{ 1 - 3\left(\frac{\omega}{u_A}\right)^2 + 6\left(\frac{\omega}{u_A}\right)^4 / g\left(\frac{\omega}{u_A}\right) \right\} \quad (\text{A.18})$$

where

$$g\left(\frac{\omega}{u_A}\right) = 1 + \left(\frac{\omega}{u_A}\right)^2 + \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{\omega}{u_A}\right) \exp\left(\frac{-u_A^2}{2\omega^2}\right) / \text{erf}\left[\left(\frac{u_A^2}{2\omega^2}\right)^{1/2}\right] \quad (\text{A.19})$$

where $\text{erf}(y)$ is the usual definition of the error function[6], and the subscript z indicates that this moment refers to the rate of collisions.

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Appendix B

Courses and Conferences Attended

In accordance with the regulations of the Department of Chemistry, University of Edinburgh, I have attended the following courses during my period of study:

1. Laser Physics
2. Recent Developments in Physical Chemistry
3. UNIX I and UNIX II
4. Vued and Micro-emacs
5. Latex

In addition, I have attended the Laser Chemistry research group meetings, departmental seminars, joint Edinburgh - Heriot-Watt laser chemistry group meetings, and the following conferences:

1. The Second Annual Northern Universities Dynamics and Spectroscopy Group Meeting, Manchester, 1991.
2. Gas Kinetics Discussion Group, York, 1991.
3. The Twelfth International Symposium on Gas Kinetics, Reading, 1992.
4. Gas Kinetics Discussion Group, Manchester, 1992.
5. Orientation and Polarisation Effects in Chemical Reaction Dynamics (a NATO Advanced Workshop) Assisi, Perugia, Italy, 1992.

Appendix C

Publications

- Velocity-averaging effects on polarisation measurements in hot atom reactions, E.P. Gilbert, G. Maitland, A. Watson and K.G. McKendrick, *J. Chem. Soc. Faraday Trans.*, **89**, 1401(1993).