THE SPECTROSCOPIC STUDY OF SIMPLE POLYATOMIC MOLECULES BY SYNCHROTRON AND LASER IRRADIATION

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A thesis submitted in partial fulfilment for the degree of
Doctor of Philosophy

University of London
2001

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Abstract

This thesis describes the spectroscopic study of simple poly-atomic molecules, for example NO and Cl₂O by UV radiation derived from synchrotron and laser sources. Synchrotron studies were carried out at the Daresbury Laboratory Synchrotron Radiation Source, and the laser studies performed at University College London.

The thesis is composed of six chapters. The first chapter discusses molecular structure; UV absorption of photons by simple molecules and describes the modern techniques of Resonance Enhanced Multi Photon Ionisation (REMPI) and Laser Induced Fluorescence (LIF) processes.

Chapter two describes the apparatus and the experimental techniques developed during this project at the Daresbury Laboratory Synchrotron Radiation Source. Details are given on the different photoabsorption cells that were built and used, as well as details of synthesis plants used to create short lived molecules of particular importance to atmospheric chemistry, for example N₂O₅.

Chapter three gives a full description of the laser system constructed to study REMPI and LIF processes. The data collection and experimental methodology of the final experimental configuration to study REMPI phenomena is also detailed.

Chapter four describes the results obtained by photoabsorption studies for the atmospheric nitrogen and chlorine oxides (Cl₂O, N₂O₅ and ClONO₂).

Chapter five gives an overview of the results obtained by photoabsorption studies of Polycyclic Aromatic Hydrocarbons.

Chapter six presents conclusions of the current work and discusses future experiments that may be undertaken in the apparatus developed during this PhD program.
Acknowledgements

Dr. Nigel Mason for his support and encouragement throughout the course of this PhD programme.

Prof. Marie-Jeanne Hubin-Franskin, Prof Jacques Delwiche, Dr. Isobel Walker, Dr. George Marston, Dr. Francoise Motte-Tollet, Dr. Jon Gingell, Dr. Bratislav Marinkovic, Marie-Paul Ska, Dr. Bruce Osborne, Dr. Shashi Pathak, Sahraoui Hadji-Ziane, Dr. Nykola Jones and Antoine Berton without whose help it would not have been possible to carry out the work at Daresbury Synchrotron Facility.

Ivan Rangué and Ted Oldfield for their excellent advice and assistance in the construction of the UCL based laser apparatus.

Dr. Ciaren Mythen, Dr. Mike McDonald, Dr. David Shaw and the support staff at the Daresbury Synchrotron Facility, for their assistance.

The EPSRC for their financial support.

My parents who have given me continuous support and to my Mother who has always been there to support me especially when I needed her most, and to my Father who has been very ill and to the rest of my family.

Particular thanks go to Jane Baker for her support during hard times, always being there when I needed her, and her help with the layout and diagrams of this thesis.

Friends and colleagues past and present at UCL: Dr. Haibo Zhao, Dr. Jon Gingell, Dr. Nykola Jones, Dr. Petra Tiegeder, William Andrew Steer, Rafal Pisula, Paul Kendall, Paulo Limao Vieira, Sam Eden, Anita Das, Silvia Bergamini, Katherine Brown, Zoe Baillie, James Perry, Robin Mukerji, Gary Martin, Roland Easton, Wilkes McDermid.

Daniel Morse, Daniel Gruner, the UCL mountaineers and all my other friends - you know who you are - just for being there and sharing good times.

And finally, a mention should go to Rafal Pisula, who always has beers and explosives when we run out!
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CHAPTER ONE
INTRODUCTION TO MOLECULAR SPECTROSCOPY

1.1 Introduction.

Optical spectroscopy has played an important role in our understanding of molecular and atomic processes. The fundamental experimental techniques used to acquire spectroscopic data have remained relatively unchanged since their first development in the 1800’s, although the light sources employed have evolved significantly. In the early days of optical spectroscopy many studies relied upon investigations of how substances absorbed light of varying wavelength. White light was passed through a sample, and a monochromator used to study relative absorption as a function of wavelength. This would enable an absorption spectrum to be measured as a function of wavelength. In an absorption spectrum, the wavelengths that correspond to photons of energies that lead to absorption will be seen as troughs in the continuum. The reduction in intensity is a result of processes that have attenuated the photon flux intensity.

A major development was the introduction of synchrotron radiation. The synchrotron emits a continuum of radiation, usually spanning from the far infra-red through to the extreme ultraviolet. Synchrotron studies rely upon the use of a monochromator and scanning mechanics to isolate narrow sequential bands of the continuum. As the monochromator scans, a spectrum of absorption versus wavelength is recorded. With improvements in monochromator resolution, the effects of line saturation, discussed in section 2.10, were reduced and so it became possible to study increasingly narrow absorption bands.
The introduction of narrow band tuneable dye lasers allowed the study of structure previously inaccessible to optical spectroscopy, such as ro-vibrational structure within molecular excited states. This was due to the fact that dye laser radiation can be wavelength selected with a resolution far greater than any previously possible with monochromator based synchrotron systems. In this chapter the use of both synchrotron radiation and laser radiation to probe molecular structure will be discussed.

1.2. Justification for the course of study taken.
Photoabsorption studies of important atmospheric chlorine and nitrogen oxides were performed to provide data that can be used to derive atmospheric photolysis rates and thus help improve the computer models used for the investigation of the mechanisms that lead to the destruction of stratospheric ozone. Photoabsorption studies of polycyclic aromatic hydrocarbons, PAH's, were performed since these are believed to be key ingredients in the synthesis of molecules in the interstellar medium, ISM. Complementary laser studies were carried out to probe the spectroscopy of NO containing molecules with very high resolution such that the absorption / emission lines can be adopted for remote sensing (satellite) investigations of global pollution.

1.3 Molecular Structure.
Molecules have a structure that is more complex than that of individual atoms due to the greater number of degrees of freedom available in a molecule (i.e. rotational and vibrational degrees of freedom) and the complex distribution of electrons that is possible when atoms share their outer valence electrons in a bound molecular state. The problem can be simplified by assuming that electrons and the much more massive nuclei, experience forces of similar magnitude. This results in nuclear motions that are very much slower than electronic motions, allowing the assumption to be made that the nuclei occupy fixed positions within the molecule and electrons move around them. Electronic and nuclear forces can then be treated independently.
Molecules consist of atoms bound together by the charge distribution of the outer valence electrons. It is the transition between energy levels of these outer electrons when absorbing or emitting energy that has allowed the field of optical spectroscopy to develop. At optical wavelengths, the inner electrons are too tightly bound to be active. However, they can be probed spectroscopically with X-rays which are of a higher energy.

Motion within a molecule consists of three modes, namely rotational, vibrational and electronic. Rotational motion may be ascribed to rotations occurring about the centre of mass of the molecule, with the nucleus remaining fixed at its equilibrium position (rigid rotator model). In practice molecular bonds are elastic and therefore are able to change length during molecular rotation, such that the molecular rotational motion becomes more complicated. Vibrational motion consists of small oscillations of nuclei about their equilibrium positions. During this kind of motion, the bond lengths may also change as well as there being changes in the bond angles. When such motion occurs simultaneously with rotational motion of the nuclei, it is known as ro-vibrational motion. Electronic motion, as the name suggests, consists of electron transitions from one energy level to another and may take place during vibrational or rotational motion.

The energy differences between the energy levels of electronic motion of the valence electrons is in the order of a few eV. Therefore, spectroscopic studies of valence electrons occurs in the visible and ultra-violet regions of the electromagnetic spectrum. The energy spacings for rotational and vibrational energy levels are in the region from 0.001 eV to 0.1 eV. Rotational structure in the ground state is therefore studied using microwave radiation, and vibrational structure with infra-red techniques. However the use of very narrow band, finely tuneable radiation, such as that obtainable from a tuneable dye laser source, allows ro-vibrational structure to be seen within the electronic structure revealed by the electronic transitions. This is shown in figure 1.1 below for the NO molecule.
1.4 Transition Selection Rules.

To allow the calculation of the probability for any given transition, one needs to know the quantum mechanical wavefunctions for the two states between which the transition occurs. The wavefunctions are only known accurately for simple systems, and therefore it is often the practice to determine whether a transition is optically allowed or forbidden (the transition probability being non zero, or zero respectively). Transitions are allowed if they satisfy the condition $\Delta l = \pm 1$, $l$ being the orbital quantum number, and typically will have lifetimes of a few ns. Transitions will result either in absorption or emission of radiation, and therefore transitions will lead to spectral lines being seen.

Molecules that do not possess a permanent electric dipole moment, that is ones that are homonuclear, eg H$_2$, do not create purely rotational or vibrational optical spectra, unless there is also a change in the electronic state. However, molecules with a permanent electric dipole, eg H$_2$O, produce purely rotational or vibrational spectra, with spectral lines being seen according to the selection rules. The selection rule for rotational transitions is;

$$\Delta J = \pm 1$$  \hfill (1.1)
\( \Delta J \) being the difference between the rotational quantum numbers of the initial and final states. The equivalent selection rule for vibrational transitions is;

\[
\Delta \nu = \pm 1 \tag{1.2}
\]

\( \Delta \nu \) being the difference between the vibrational quantum numbers of the initial and final states.
Vibrational transitions are accompanied by changes in the rotational state, which is governed by the rotational selection rule stated.

For molecules containing more than one electron, the electronic transition rules are as follows:

\[
\Delta \Lambda = 0, \pm 1 \tag{1.3}
\]

\( \Lambda \) being the orbital angular momentum,

\[
\Delta S = 0 \tag{1.4}
\]

\( S \) being the spin momentum,

\[
\Delta \Omega = 0, \pm 1 \tag{1.5}
\]

\( \Omega \) being the total angular momentum.

1.5 Rotational Excitation.
Rotational states of molecules can be very complex, especially for three dimensional molecules, when various rotational states can co-exist within a molecule. For a given molecule, calculations are simplified by resolving rotational motion into three components about three mutually perpendicular axes passing through the centre of mass.
This allows three mutually perpendicular moments of inertia to be defined for the molecule, namely \( I_A, I_B \) and \( I_C \). The system is further simplified by dividing molecules into four distinct categories, defined by the molecular shape and relative values of \( I_A, I_B \) and \( I_C \). These categories are defined as follows;

1. linear molecules for which \( I_A = 0 \) and \( I_B = I_C \) e.g. \( \text{O}_2 \)

2. symmetric tops for which \( I_A \neq 0 \) and \( I_B = I_C \neq I_A \) e.g. \( \text{CH}_3\text{Br} \)

3. spherical tops for which \( I_A = I_B = I_C \) e.g. \( \text{CH}_4 \)

4. asymmetric tops for which \( I_A \neq I_B \neq I_C \) e.g. \( \text{H}_2\text{O} \).

The energy levels for rotational states of a rigid (fixed internuclear distance) molecule are given by;

\[
E_J = \left( \frac{\hbar^2}{8\pi^2 I} \right) J(J+1)
\]  
(1.6)

or \( \varepsilon_J = \frac{E_J}{\hbar c} = BJ(J+1) \)  
(1.7)

\( \hbar \) being Planck’s constant, \( I \) the moment of inertia, \( J \) the rotational quantum number \((J = 0, 1, 2, \ldots)\), \( \varepsilon_J \) the wavenumber, \( c \) the speed of light and \( B \) the molecular rotational constant, given by;

\[
B = \frac{\hbar}{8\pi^2 I_c} = \frac{\hbar}{8\pi^2 \mu r^2 c}
\]  
(1.8)

\( \mu \) being the reduced mass and \( r \) the bond length. The allowed transitions are set by the selection rule: \( \Delta J = \pm 1 \), such that the wavenumbers of the allowed transitions are given by;
\( \varepsilon_{j \rightarrow j+1} = B(J+1)(J+2) - BJ(J+1) = 2B(J+1) \) \hspace{1cm} (1.9)

This selection leads to absorption spectra, for rigid diatomics, having lines at 2B, 4B, 6B, ... being brought about by transitions from \( J=0 \) to \( J=1 \), \( J=1 \) to \( J=2 \), etc.

This is a simplified treatment, as in reality the molecules are not fully rigid, and internuclear distances increase as the molecular rotation speed increases, due to the centrifugal force. The change in internuclear separation with varying rotation speed is taken into account by a correction factor, \( D \), the centrifugal distortion constant, which is added into the wavenumber equation, such that;

\[ \varepsilon_j = BJ(J+1) - DJ^2(J+1)^2 \] \hspace{1cm} (1.10)

\( D \) being given by;

\[ D = \frac{\hbar^3}{32\pi^4I^2r^2kc} \] \hspace{1cm} (1.11)

\( k \) being the force constant, given by;

\[ k = 4\pi^2\omega^2c^2\mu \] \hspace{1cm} (1.12)

\( \omega \) being the frequency of rotation.

The rotational transition energies for the non-rigid rotator model are only slightly less than those for the rigid rotator, and these differences only become significant for \( J \geq 5 \). This is shown diagrammatically in figure 1.2 below.
Figure 1.2 The rotational energy levels of the rigid and non-rigid models for a diatomic molecule (Banwell, 1983).
1.6 Vibrational Excitation.
Vibrational excitation arises when the energy incident upon the molecule causes the nuclei to oscillate about a mean position, rather than remaining in a fixed position. The equilibrium position is determined by the balance of forces acting on the nucleus namely: (1) the repulsion between positively charged nuclei, (2) the repulsion between negatively charged inner electrons around the nucleus and (3) the attraction of the nucleus to the electrons around another nucleus. The molecular energy is at a minimum when there is a balance between these forces. The bond length is defined as the distance between atoms whilst at their equilibrium separation.

The relationship between bond length and energy is shown in figure 1.3 below.

![Figure 1.3. The potential energy curves for rigid (dashed line) and non-rigid (solid line) rotors (Bransden and Joachain, 1983).](image-url)
The lowest vibrational states of a diatomic molecule exhibit nuclear motion which is approximated by simple harmonic motion, SHM, represented by the dashed line in figure 1.2 above.

For SHM, the vibrational energies for the various quantum numbers, \( v \), are given by:

\[
E_v = (v + 1/2)\hbar \omega_{osc}
\] (1.13)

\( v = 0, 1, 2, \ldots \), \( \hbar \) is Planck’s constant and \( \omega_{osc} \) is vibrational oscillation frequency. The lowest vibrational energy occurs when \( v = 0 \) giving \( \frac{1}{2}\hbar \omega_{osc} \) (the zero point energy), the vibrational energy levels being spaced equally with intervals of \( \hbar \omega_{osc} \), such that the selection rule for this simple harmonic model becomes \( \Delta v = \pm 1 \).

In practice, however, real molecules do not behave as simple harmonic systems. If a bond between molecules is stretched far enough to break, the molecule dissociates. This is represented by the solid line, in figure 1.3, which shows the relation between energy, \( E(r) \), and internuclear distance, \( r \), for a non-rigid diatomic molecule. The plot is in agreement with the empirical expression, the Morse Function:

\[
E(r) = D_{eq} [1 - \exp\{a(r_{eq} - r)\}]^2
\] (1.14)

\( D_{eq} \) being the dissociation energy, \( a \) the molecular constant and \( r_{eq} \) the bond length.

The vibrational energy levels are then given by;

\[
E = (v + 1/2)\hbar \omega_{osc} - (v + 1/2)^2 \hbar \omega_{osc} \chi_e
\] (1.15)

\( \chi_e \) being the molecular anharmonicity constant, which is small and positive giving rise to vibrational energy levels closer to one another with increasing \( v \), as shown in figure 1.3.
The selection rules for the anharmonic oscillator are $\Delta \nu = \pm 1, \pm 2, \ldots$. The larger the energy difference of a transition, the smaller the probability that the transition will occur. The transition frequency between $\nu=0$ and $\nu'=1$ is the fundamental frequency, and transitions to higher levels, that is $\nu = 0$ to $\nu' = 2, 3, 4, \ldots$ are known as overtones.

When a diatomic molecule changes its vibrational energy state, the change must also be accompanied by a change in the rotational state. During the time it takes to complete a single rotation, a molecule may vibrate hundreds or even thousands of times. This allows the vibrational and rotational motions to be treated separately, such that the total energy of the system is the sum of the vibrational and rotational energies, given by:

$$E_{J,u} = E_J + E_u$$  \hspace{1cm} (1.16)

$$E_{J,u} = B\hbar c(J+1) + (\nu+1/2)\hbar\omega_{osc} - (\nu+1/2)^2 \hbar\omega_{osc} \chi_e - D\hbar cJ^2(J+1)^2$$  \hspace{1cm} (1.17)

The centrifugal distortion term, $-D\hbar cJ^2(J+1)^2$, may often be omitted as its effect is negligible in comparison to the other terms in equation 1.17 (for small $\Delta J$).

The combined rotational and vibrational selection rules for a diatomic molecule are equivalent as those for the separate rotational and vibrational motions;

$$\Delta \nu = \pm 1, \pm 2, \ldots \text{ and } \Delta J = \pm 1$$  \hspace{1cm} (1.8)

For the fundamental transition, $\nu=0$ to $\nu=1$, which has the greatest probability of occurrence, the transition energies for combined rotational and vibrational motion are given by:

$$E_{J,u} = \hbar\omega_{osc}(1-2\chi_e) + 2B\hbar c$$  \hspace{1cm} (1.9)
with \( m = \pm 1, \pm 2, \ldots \). These restrictions give rise to a spectrum which consists of equally spaced lines, of spacing \( 2B \), on each side of the band origin \((=\hbar \omega_{osc}(1-2\chi_e))\). Lines on the low frequency side, for which \( m \) is negative and \( \Delta J = -1 \), are referred to as the P branch, whereas those on the high frequency side, for which \( m \) is positive and \( \Delta J = +1 \), are referred to as the R branch, the band frequency itself, where \( m = 0 \) and \( \Delta J = 0 \), is called the Q branch. The Q branch is absent from the spectra of a diatomic molecule, as \( \Delta J = 0 \) transitions are forbidden.

This is depicted diagrammatically below in figure 1.4

![Diagram](image)

Figure 1.4 The P, R and Q spectral branches shown for a hypothetical spectrum. (Banwell, 1983). The dashed line indicates the band origin.
The number of fundamental vibrational frequencies for a molecule composed of \( n \) atoms is given by \( 3n - 6 \) for a non-linear molecule and \( 3n - 5 \) for a linear one. The number of bond stretching modes is given by \( n - 1 \), the rest being vibrations which involve bending of the bonds. A typical molecule is NO\(_2\), which is a non-linear triatomic and has three \((3n - 6)\) allowed vibrational modes, of which two are stretching modes which involve changes of bond lengths around an equilibrium length. The third is a bending mode where the bond lengths remain fixed, but the bond angle changes. These vibrations are categorised as \( \nu_1, \nu_2, \nu_3 \), in order of symmetry type. The highest frequency of vibration is that of the symmetric stretch, \( \nu_1 \) the next highest is that of the bending mode, \( \nu_2 \), the lowest being that of the asymmetric stretch, \( \nu_3 \). The three fundamental modes of vibration for a triatomic, such as O\(_3\), are shown in figure 1.5 below.

Figure 1.5. The three fundamental vibrational modes for O\(_3\).
A process useful for the study of vibrational modes is photonic absorption. This involves the absorption of a photon (energy $h\omega$), which causes the molecule to be excited from state a to state n, after which the molecule de-excites from state n to another state b, during which it emits a photon of energy $h\omega'$. If the energy of the two states is the same, that is $\omega=\omega'$, the scattering process is known as Rayleigh Scattering. However, if the energy of the states differs, the process is known as Raman Scattering, and is useful in the study of vibrational and rotational motion of molecules. For $\omega>\omega'$, the scattered radiation is known as Stokes Radiation, and for scattering where $\omega<\omega'$, the scattered radiation is known as anti-Stokes radiation.

1.7 Electronic Excitation.

The electrons in atoms and molecules are distributed within the orbits according to the internal energy of the atom or molecule. The electrons can move between orbits, and when they do, the process is accompanied by the emission or absorption of a photon. The molecular state excitation energy lies between about 1 eV and 10 eV, the corresponding photon energies are in the visible and ultraviolet parts of the electromagnetic spectrum. For this reason, electronic spectra for molecular systems are studied using visible light through to the far UV. The ground state configuration of molecules is usually singlet, and since the selection rule $\Delta S=0$ only allows transitions to take place between states of the same spin multiplicity (i.e. singlet $\rightarrow$ singlet, doublet $\rightarrow$ doublet, etc) transitions are usually only allowed to states which are also singlets, however in some cases, the ground state is a doublet, (such as OCIO), triplet, or even a quartet. Electronic transitions can be accompanied by changes in vibrational and/or rotational state, such that during such a transition, the change in the internal energy is:

$$\Delta E_{e,v,j} = (E_{e'} + E_{v'} + E_{j'}) - (E_e + E_v + E_j)$$  \hspace{1cm} (1.20)

$E_{e'}, E_{v'}, E_{j'}$ being the energies of the excited electronic, vibrational and rotational states, and $E_e + E_v + E_j$ being the equivalent energies of the initial states.
The Franck Condon principle states that the duration of an electronic transition is short in comparison to the period of vibrational oscillation, such that the bond length of molecules do not change appreciably during such transitions. This allows the electronic transitions between states to be illustrated as straight lines, that is ones of fixed $r$, the internuclear distance or bond length, on an energy/bond length diagram. This is illustrated in figure 1.6 below, with lines illustrating electronic transitions between states A and B shown.

![Diagram of Franck-Condon principle](image)

Figure 1.6 An illustration of the Franck-Condon principle (Brandsen and Joachain, 1983).

The probability distributions for the vibrational states as a function of internuclear distance, $r$, are shown in figure 1.7 below. For the $\nu=0$ state, the most probable
Internuclear distance is the equilibrium distance, i.e. the bond length. For the higher vibrational states the most probable internuclear distance lies at either at the maxima or minima.

![Diagram](image)

Figure 1.7 The probability distribution for the vibrational states of a diatomic molecule as a function of the internuclear distance, $r$. The maxima in the probability curves represent the most likely internuclear distances for the molecule (Banwell, 1983).

The potential energy curves for differing electronic states often have different equilibrium distances, hence a vertical line joining the two states, representing a transition, will often join differing vibrational levels for the two electronic states. If a transition takes place between a low electronic state such as A and a higher electronic state B, the molecule may dissociate if the vertical line joining the two states on the potential energy curve crosses state B at an energy greater than the dissociation energy.
of state B. This is known as dissociation from a bound state. At energies at and above the dissociation energy of state B, there will be seen a continuum, a wide feature with no structure, in the spectrum. This is shown schematically in figure 1.8 below. Also, a continuum will be seen when excitation occurs from state A or B to a higher repulsive state C, as this will also result in molecular dissociation, this being known as dissociation from a repulsive state. This is also shown in figure 1.8.

![Dissociation by excitation](image)

Figure 1.8. Dissociation by excitation into a stable upper state B, and a continuous upper state C (Banwell, 1983).

In cases where the potential energy curves for states B and C cross, spectral lines arising from transitions between states A and B can become broadened by a process known as predissociation, whereby a B state transfers to the C state by radiationless transfer, as the process does not involve an energy change at the point of intersection, $i$, of the two potential energy curves. This is shown in Figure 1.9 below.
1.8 Rydberg and Valence States.

The two main types of excited electronic states that a ground state molecule can be excited to are valence states and Rydberg states. Generally, the atomic orbitals that combine to form the molecular orbitals define the valence shell for that molecule. For example the filled orbitals of ground state of ozone consist of 2s and 2p orbitals, such that the valence shell of ozone is at n=2, n being the principal quantum number. Excitations into the unfilled orbitals that are generated by the valence shell atomic orbitals are known as valence transitions. Transitions that occur into orbitals that have a higher principal quantum number are known as Rydberg transitions, for example transitions into the n>=3 orbitals for ozone. Typically Rydberg state orbitals are an order of magnitude larger than the ground state orbitals for any given molecule.

Figure 1.9. Pre-dissociation caused by a radiationless transition from state B to state C.
Most molecular valence shell orbitals fall into one of three categories. These are \( \sigma \) orbitals, \( \pi \) orbitals and \( n \) (non-bonding) orbitals. A bond that holds atoms together by accumulation of charge between the nuclei is termed a \( \sigma \) bond and has \( \sigma \) orbitals. A bond that holds atoms together by the electrons accumulating alongside the nuclei is called a \( \pi \) bond and consists of \( \pi \) orbitals. Generally, electrons comprising \( \sigma \) orbitals are bound more strongly to the nucleus than electrons in \( \pi \) orbitals and \( n \) orbitals. Therefore more energy is required to cause electrons in \( \sigma \) orbitals to undergo transitions. Usually, but not always, electrons in \( n \) orbitals are less strongly bound than those in \( \pi \) orbitals. The spectral regions where valence transitions are expected are shown in figure 1.10 below.

Transitions that occur into Rydberg states are usually observed above about 7eV. A Rydberg state can be thought of as an electron in a large radius orbital, travelling around a central core consisting of the nuclei and remaining occupied molecular orbitals. Rydberg states containing the same molecular ion core are related as their potential energy surfaces are defined by that of the molecular ion, this being exemplified by the Rydberg formula, shown in equation 1.21 below.

\[
E_{\text{excitation}} = E_{\text{ionisation}} - \frac{R}{(n-\delta)^2}
\]  

(1.21)
R being the Rydberg constant (13.6 eV), n the principal quantum number of the upper Rydberg orbital, and δ the quantum defect. The quantity $E_{\text{excitation}} - E_{\text{ionisation}}$ is referred to as the term value, and is often used when discussing Rydberg states. Rydberg states closely resemble those of atomic orbitals, that is they consist of an outer electron in an orbital similar to an atomic orbital, the difference being that it is orbiting a molecular ion instead of an atomic core. Therefore, it follows logically that Rydberg states are labelled up as ns, np, nd etc, in correspondence to their distribution around the molecular ion. Quantum defects are a measure of the penetration of the outer Rydberg orbital into the central core, and is dependant upon the shape of the orbital. Rydberg s orbitals (δ usually ~1) penetrate more than p orbitals (δ usually ~0.6) which penetrate more than d orbitals (δ usually ~0).

1.9 Experimental Methods for Probing Molecular Spectra.


Photoabsorption spectroscopy was one of the earliest forms of spectroscopy developed, and is concerned with the degree of attenuation of light by a sample of interest. The light source can either be a lamp, or more recently a synchrotron. The light is wavelength selected and attenuation by the sample as a function of wavelength is measured. Troughs in the spectrum correspond to wavelengths where attenuation occurs as a result of excitations. Since its conception it has evolved considerably, with the development of synchrotron sources and better monochromators allowing the probe radiation to have a narrower bandwidth. Photoabsorption spectroscopy is discussed in further detail in Chapter 2.
1.9.2 Resonance Enhanced Multi-Photon Ionisation (REMPI) and Laser Induced Fluorescence (LIF) Spectroscopy.

**REMPI process.**
The development of laser REMPI and LIF spectroscopy has allowed the probing of molecular systems at resolution much higher than those possible with synchrotron based spectrometers. REMPI is the process that accesses ionised states of molecules or atoms by the simultaneous excitation of molecular states by more than one photon. The cross section for simultaneous absorption of two or more photons by a molecule is very low, however the low cross section can be compensated for by using light of high intensity, as that of a laser. Small molecules composed of light atoms typically have ionisation energies of around 10-15 eV, which corresponds to the absorption of two short wavelength UV photons. The cross section of the absorption process is greatly enhanced if there is a real excited state at the energy of one or two absorbed photons. REMPI can either be achieved by using a single wavelength laser, labelled (1+1), (2+1), (1+2), (2+2), where the number indicates the number of exciting photons, or using two lasers, of different wavelengths, where a prime is used to denote the different wavelengths, as (1+1’), (2+1’), (1+2’), (2+2’) (McKeachie J.R, awaiting publication). Excitation by the first photon causes the molecule to go from the ground state to an excited vibrational or ro-vibrational state, from where the second photon supplies an excess of energy that causes ionisation of the molecule’s valence electron. The REMPI scheme used in the work outlined in this thesis was (1+1).

The process is shown diagrammatically in figure 1.11 below:
Figure 1.11. Representation of transitions that occur in REMPI processes.
The cross section for absorption of photons of energy $h\nu_1$ and $h\nu_3$ is very low, and so will not contribute to the REMPI spectrum observed. The cross section for the absorption of photons of energy $h\nu_2$ is high, as the transitions are to a Rydberg state, and these will give rise to a strong signal in the REMPI spectrum observed.

**LIF process.**
LIF is the acronym for a process whereby a stimulating photon creates an excited molecular atomic or ionic state, which then reverts to its original state either directly or indirectly, and releases a photon with a quanta of energy less than or equal to that of the exciting photon.

A schematic diagram of the LIF process is shown in figure 1.12 below.
Figure 1.12 Representation of transitions that occur in LIF processes. An exciting laser photon, of energy $h\nu_1$ creates an excited state, from where energy is lost by the emission of a photon of energy $h\nu_2$, observed as the LIF photon, and then energy is lost either by radiationless transfer or by the emission of a further photon, the system dropping to the ground state.

1.9.3 Electron Energy Loss Spectroscopy.

Electron energy loss (EEL) spectroscopy involves the excitation of a molecule in a collision with an electron of well defined energy, $E$, and can be described with the following equation:

$$XY + e^-(E) \rightarrow XY^* + e^-(E-\Delta E)$$ (1.22)

$XY$ being a ground state species, $(E)$ the energy of the incident electron, $XY^*$ the excited species, and $\Delta E$ the energy lost by the electron in the collision. To obtain an EEL spectrum, electrons of known energy are fired at a target gas, and the electron current, as a function of energy loss, $(\Delta E)$, is measured, resulting in a spectrum which displays the excitation cross section of the compound as a function of electron energy lost (EEL).
1.9.4 Photoelectron Spectroscopy.

Photoelectron spectroscopy involves the observation of the electrons emitted by atoms and molecules when they are photoionised. When a molecule is ionised by photons of energy $\hbar \omega$, the emitted electrons will have an energy given by:

$$E_e = \hbar \omega - IE$$

(1.23)

$E_e$ being the electron energy, and $IE$ the ionisation energy of the molecule. The electron is a carrier for the excess energy of the photon, that which remains after energy transfer to the molecule during ionisation. For a given polyatomic molecule the number of ionisation energies will be equal to the number of molecular orbitals, and each will lead to a band structure observed for the molecular ion. This allows the energy analysis of the emitted electrons to reveal the band structure of the molecular ion, and therefore give the ionisation energies of the neutral molecule. The band profiles determined can be used as an aid to assign Rydberg states as the origin of the structure is from the same central molecular ion core, and so photoelectron and photoabsorption spectra are related.

1.10 Summary.

In this chapter I discuss basic molecular spectroscopy. Optical excitation of rotational, vibrational and electronic states is discussed. The Franck-Condon principle and dissociation pathways are described, and finally experimental methods used to study molecular spectroscopy are outlined. In this thesis I used synchrotron radiation and laser radiation to study molecular species in the UV-Vis region of the electromagnetic spectrum.

In the next two chapters I will discuss the experimental methods used in the synchrotron and laser studies. In Chapters 4 and 5 the photoabsorption results for atmospheric nitrogen oxides and Polycyclic Aromatic Hydrocarbons will be presented. Chapter 6 presents the results from the laser work and suggested future work.
CHAPTER TWO
MEASUREMENT OF PHOTOABSORPTION CROSS SECTIONS
BY MEANS OF SYNCHROTRON RADIATION

2.1 Introduction.
This chapter gives an overview of the experimental work carried out at the Daresbury Laboratory Synchrotron Radiation Source. The evolution of the photoabsorption apparatus used is described, with reasons for improvements and modifications made as a result of experimental experience gained during the course of this project.

2.2 Synchrotron Radiation and Applications.
Synchrotrons provide a means of studying a wide range of phenomena, ranging from X-ray diffraction to molecular photabsorption. The research described in this thesis is concerned with the electronic configurations of molecules in their various states. In the work presented in this thesis, the ultraviolet band of the emitted light from a synchrotron has been used to study valence and Rydberg states of simple molecules, providing data complementary to that obtained using laser techniques.

2.3 Synchrotron Radiation.
Synchrotron radiation is the radiation emitted tangentially when charged particles travelling at relativistic speeds are made to accelerate. In a synchrotron, the acceleration of particles is achieved by causing the particles to change their trajectory whilst maintaining constant speed. Their trajectory is constantly changed by containing them in a circular orbit, thereby providing a means of acceleration, resulting in the emission of synchrotron radiation. The resulting radiation is very intense, highly collimated and polarized in the plane of the orbit. It is for these reasons that synchrotrons are often the
light sources of choice used by spectroscopists requiring high intensity radiation ranging from the far infrared through to hard x-rays.

The synchrotron energy radiated (E) per orbital revolution of a particle of rest mass \( m_0 \) with a kinetic energy of \( T \) is given by:

\[
E \propto \left( \frac{T}{m_0 c^2} \right)
\]

Hence for a given kinetic energy, the synchrotron radiation emitted by lighter particles is of a higher intensity than that which is emitted by heavier particles, as for a given kinetic energy, lighter particles will be travelling at a higher velocity than particles with a higher mass. This property of synchrotrons is exploited where the main purpose of the synchrotron is to provide a source of photons, with electrons or positrons being used as the light particles.

**2.4 The Daresbury Laboratory Synchrotron Radiation Source.**

The Synchrotron Radiation Source (SRS) at the Central Laboratory of the Research Councils (CLRC) at the Daresbury site was built in the 1970s on the site of a former electron storage ring. It has the capability of providing a continuous spectral emission from the far infrared through to short wavelength hard x-rays (Daresbury Online, 2001).

The SRS is composed of three separate particle accelerators. The first is a linear accelerator (LINAC) which accelerates low energy electrons to 12 MeV and injects them into a booster synchrotron. The booster accelerates them to 600 MeV and injects precisely timed bunches into the main storage ring (the SRS itself). Once a sufficient number of bunches has been injected into the SRS to constitute a suitable operating current (usually around 200 mA), injection is ceased and the bunches are further accelerated until individual electrons making up the ring current have an energy of 2 GeV. Acceleration is achieved by means of a high frequency electric field whose frequency is increased to ensure that electrons of increasing velocity arrive at the correct instant to be further accelerated. Once the maximum energy of 2 GeV has been reached, the frequency of the field is locked and maintained constant. At 2 GeV the electrons are
travelling at 99.999997 percent of the speed of light and have a relativistic mass equivalent to around 4000 times that of their rest mass.

The electrons are in fact not maintained in a truly circular orbit. This would be difficult to achieve and more importantly would result in an isotropic emission of synchrotron radiation in the plane of the orbit, which would lead to unused radiation as collection of photons along the entire length of the circular orbit would be uneconomical. The electrons actually travel in straight paths where they do not experience any acceleration. A “circular” orbit is achieved by causing small but tight changes in the trajectories of the electrons, resulting in an overall closed orbit. It is at the points where the trajectory changes that the electrons experience acceleration and therefore emit synchrotron radiation. The electrons path is altered this way 16 times around the orbit by means of 16T bending magnets. Quadrupole and sextupole magnets are also used to maintain beam stability around the storage ring. The ring also contains two wigglers and an undulator; these are super-conducting magnets with high fields of around 5 T causing sharp changes in trajectory, giving higher intensity X-ray emission at these magnets.

A schematic of the accelerators at the Daresbury SRS site is shown in figure 2.1. A summary of the energies at the various stages of the synchrotron, and available range of photon energies is given in table 2.1

The synchrotron radiation emitted at each magnet is passed onto experimental stations, known as beam lines, by a series of mirrors. Photoabsorption work detailed in this thesis was carried out at Beam Line 3.1, and this will be described in the next section.
Figure 2.1 Daresbury SRS Site Layout. Electrons are accelerated in the Linear Accelerator, LINAC, to an energy of 12 MeV. They are then injected into a booster synchrotron, where they are accelerated further to an energy of 600 MeV, from where they are injected into the main synchrotron ring where they are accelerated to 2 GeV and maintained at this energy whilst the current drops off with time due to collisions with particles in the not-absolute vacuum conditions.

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<th>Current /mA</th>
<th>Electron energy /MeV</th>
<th>Photon energy /eV</th>
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<td>12</td>
<td>-----</td>
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<td>Beam lines</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>6 - 200,000</td>
</tr>
</tbody>
</table>

Table 2.1 Available energies at the Daresbury Synchrotron.
Plate 2.1. View of main synchrotron buildings from the roof of the decommissioned Van de Graaf accelerator tower.

2.5 Beamline 3.1.

This consists of a means of accessing wavelength selected synchrotron radiation, using the Seya Monochromator, and a means of carrying out photoabsorption measurements, using the Daresbury Laboratory Molecular Science Absorption Apparatus, DLMSAA. The Seya Monochromator and associated systems are Daresbury owned and maintained, whilst the Absorption Apparatus is becoming UCL owned and maintained, as more and more modifications are carried out and funded by UCL.

A schematic of Beamline 3.1 is shown in figure 2.2 below.
Although strictly speaking, the beamline is only that part of the apparatus which remains unchanged from study to study, 3.1 has been predominantly used for the acquisition of Photoabsorption Cross Sections, and so the entire apparatus appears as 3.1 above.

2.6 The SEYA monochromator.

The SEYA monochromator is the fundamental component of beam line 3.1 at the SRS. The beam line experimental configuration delivers wavelength-selected synchrotron radiation to the experimental area by means of a series of mirrors, slits, and the monochromator reflection grating. A narrow band of the continuous spectrum emitted by the synchrotron is selected by the monochromator by the use of narrow slits and the grating. The grating disperses the mixed wavelength incident light into an angular distribution of wavelengths according to the relation:

$$\sin \theta = p \lambda / d$$  \hspace{1cm} \text{at maxima positions} \hspace{1cm} (2.2)$$

$\theta$ being diffraction angle of light of wavelength $\lambda$, $p$ the order of diffraction, and $d$ the grating line separation. The zero order light from the grating is in fact specular reflection and contains a mixture of all wavelengths. It is the first order light that is of use to experimentalists as it contains narrow band radiation of the highest intensity. In general,
the longer the wavelength of incident light, the greater the diffraction angle. This is true for all orders observed. This is shown schematically in figure 2.3.

![Diagram of diffraction of light by a reflection grating](image)

Figure 2.3 Diffraction of light by a reflection grating

In the SEYA monochromator the angles of the second order short wavelengths were found to correspond with the angles of the longer wavelengths of the first order light. The contributions of second order maxima to first order maxima were minimised by the use of a carefully designed grating the first order maxima being considerably more intense than the second order maxima.

To gain access to different wavelengths using the monochromator the angle at which diffracted light is “observed” relative to the grating has to be varied. In practice this is achieved by rotating the grating whilst collecting diffracted light via an exit slit. The slit width determines the monochromator transmission bandwidth. In practice, the entry slit is usually set to 1.5 mm and the exit slit to 1mm. The narrower the slit, the smaller the bandwidth and the higher the achievable resolution of the photoabsorption spectrometer.

The Seya Monochromator has three interchangeable gratings, allowing high resolution experiments to be carried out in specific wavelength ranges.

Table 2.2 shows the parameters for the three gratings, and the monochromator and associated apparatus is shown in plate 2.2 below:
<table>
<thead>
<tr>
<th>Grating</th>
<th>Wavelength Range</th>
<th>Grating Lines/mm</th>
<th>Peak Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low energy</td>
<td>120 – 500nm</td>
<td>600</td>
<td>170 nm (7.3 eV)</td>
</tr>
<tr>
<td>Medium Energy</td>
<td>60 – 250nm</td>
<td>1200</td>
<td>80 nm (15.5 eV)</td>
</tr>
<tr>
<td>High Energy</td>
<td>40-120</td>
<td>1200</td>
<td>55 nm (22.5 eV)</td>
</tr>
</tbody>
</table>

Table 2.2. Grating parameters for the Seya Monochromator.

Plate 2.2. The SEYA monochromator and beamline. Note at the foot of the plate the ClONO₂ synthesis apparatus on a trolley.

2.7 The Daresbury Laboratory Molecular Science Absorption Apparatus.

All the Daresbury studies outlined in this thesis are based on work carried out using various forms of absorption apparatus, which are used in conjunction with Beam line 3.1. These rely on passing light through a gas filled cell, and measuring the attenuation of the light, this attenuation being proportional to the absorption cross section of the gas. During the time of the research carried out, the design of the gas cell evolved from a simple static cell to a more advanced windowless flow cell. The history of this evolution and detailed outlines will be given the following sections.
The Daresbury Laboratory Molecular Science Absorption Apparatus is used by our research group for the acquisition of Absorption Cross Sections of molecules of spectroscopic interest. The process of absorption is defined by the Beer Lambert Law, which states that the amount of light absorbed by a sample depends on the path length, \( l \), number density, \( n \), and sample cross section, \( \sigma \). The relationship between these is shown by the Beer-Lambert Law below:

\[
\frac{I_t}{I_o} = \exp^{-n l \sigma}
\]  

(2.3)

\( I_t \) being cell transmission intensity with sample present, and \( I_o \) transmission with no gas present.

Of interest to spectroscopic calculations is the cross section, which can be expressed as follows:

\[
\sigma = \ln\left(\frac{I_o}{I_t}\right)(1/nl)
\]  

(2.4)

This equation is particularly useful as it allows the cross section to be calculated from a knowledge of path length, number density (from a pressure and temperature reading using \( pV=nRT \)), and transmission, which can all be easily measured.

2.8 The Photoabsorption Cells.

Apparatus that is common to all the types of cell used is the Seya Monochromator, vacuum lines enclosing the absorption cell, and the photomultiplier tube and data acquisition system. The differences between the various systems used were those of cell design. For this reason, the generic apparatus is discussed in the following paragraph, with each different type of cell being given a separate sub-section.

All the cells used in the absorption studies rely upon passing synchrotron radiation through a cell, whose path length is known and measuring the intensity of light exiting the cell by means of a photomultiplier tube. The light used in these studies is in the ultraviolet part of the electromagnetic spectrum, where the quantum efficiency of the
photomultiplier tube used is low. To increase the experimental efficiency of the photomultiplier tube, the inner surface of the apparatus exit port window is coated with sodium salicilate, a substance which fluoresces blue/green in the presence of ultraviolet light. The exit port is made of glass, which absorbs strongly in the UV, but which is almost fully transparent to the visible blue green light. For this reason, the fluorescent coating is on the inner, vacuum, side of the window.

Synchrotron light is passed onto the cell via a series of mirrors, slits and a monochromator. To align the light beam to pass through the major axis of the cell, mirrors before and after the monochromator need to be adjusted. The mirror between the monochromator and the cell usually does not need to be adjusted, only minor adjustments being necessary to the mirror before the monochromator. Two micrometer screws make adjustments to the beam within a solid angle. Translational adjustment is not possible by beam line users, and if this is necessary, the height of the absorption apparatus needs to be changed. The apparatus is said to be aligned when the light exiting the sodium salicilate window does so within a few millimeters of the central part of the window. To view this light, a partially transparent piece of white material is placed up against the exit port window, allowing exiting beam to be clearly seen, and the micrometer screws are adjusted until a satisfactory beam position is achieved.

The above alignment is required for all types of cell. Additional alignment that is required for the windowless capillary flow cell will be described in the section relevant to that type of cell.

2.8.1 The Static Absorption Cell.

This is a basic cell which can be evacuated and then filled with a sample gas, with no provision for flowing the sample gas. The pressure in the cell and surroundings is reduced by means of a turbo molecular drag pump, commonly known as a turbo-pump. The exhaust of this type of pump is removed by a backing pump. Backing pumps are standard impeller type rotary pumps which reduce system pressure to a level at which turbo-pumps can operate, usually 10E-2 mBar, and maintain exhaust removal once the turbo-pump is running. The turbo-pump is essentially a small gas turbine, which rotates at very high frequency, applying a drag force on low pressure gases. Turbo-pumps can attain optimal vacuums in the region of 10E-11 mBar.
The most basic design for the static cell is one where essentially a commercially available six way cross adapter is used as a cell. A pressure gauge is mounted at the top, pumping line at the bottom, gas inlet line on one side and a pair of lithium fluoride gate valves used such that light can enter via one, from one side of the cross, and leave from the other, on the opposite side of the cross. The remaining arm is simply sealed with a blanking plate. The use of lithium fluoride windows permits transmission in the VUV part of the spectrum, down to 11.27 eV (110 nm). The path length of the cell, l, is 16 cm. This is a basic design and has no provision for the control of sample temperature. A schematic of the cell is shown in figure 2.4 below.

![Figure 2.4 The basic static absorption cell.](image)

Initially, the cell is evacuated by opening the knife valve, to pump away any gases that may be in the cell. The knife valve is then closed and a sample gas admitted by means of a needle valve, until a pressure is reached that is close to the required value. At that point the valve is shut off, the pressure allowed to stabilize, and a note made of the actual pressure reached (it is very hard to achieve a pressure exactly that which is required, but as there is a pressure term in the equation used, that is not important).
2.8.2 Basic Flow Cell.
This cell is based very much on the basic cell, the only difference being that the sample
gas is continuously admitted, and pumped away via the knife edge valve. The path
length for this cell is also 16 cm. Due to being essentially the same as the basic cell in
all but mode of operation, a diagram is not given for this cell.

2.8.3 The Temperature Controlled cell.
This cell was not actually used for controlling the temperature of the sample gas. It was
however used in place of the static cell due to window contamination problems with the
basic cell. This cell will be used in future studies, especially with high melting point
compounds, such as the Polycyclic Aromatic Hydrocarbons, PAHs, that caused
considerable condensation problems in these studies.
The cell is essentially a double jacketed pipe that is suspended from a rotatable flange
mounted in a large vacuum chamber. A refrigerant or heating liquid is passed through a
feedthrough to allow control of the cell temperature. The cell has a centrally mounted
pipe that is used to fill it with sample gas, by means of evacuation and subsequent
introduction of gas until the required pressure is reached. The windows are of LiF for
similar transmission characteristics to the simple cell, and are mounted such that their
replacement is fairly straightforward.

The cell has a limitation being a static cell, as this allows any products of reaction to
accumulate, rather than be replaced by new sample as is the case for a flow cell. This is
of no consequence for inert compounds, but can be a source of error where the
compound under study slowly reacts in the cell, allowing reaction products to
accumulate. Another problem associated with this cell is that the lack of window heating
allows material to condense on the windows, which leads to unquantifiable results, as no
parameters, such as thickness of condensate, are known for the condensed material. The
problems of condensation are eliminated with the use of a windowless cell, as described
in section 2.7.5
A schematic diagram of the cell is shown in figure 2.5, and in plate 2.3 below.
Figure 2.5 The temperature controllable cell, with LiF windows.

Plate 2.3. The temperature controlled cell.
2.8.4 The Reactive Compound Flow Cell.

The reactive compound cell uses the same large chamber and top flange as the temperature controlled cell, the main differences being that the cell is made only of glass, sample gas flowing is possible, but at present temperature regulation is not possible. Since a flow cell allows for easy purging, and also permits the study of reactive transient species that may break down during the lifetime of a scan. This is advantageous because not only does it allow the study of compounds that may otherwise decompose, but also prevents reaction products from contaminating the absorption path. A schematic diagram of the cell is shown in figure 2.6 below.

![Diagram of the Reactive Compound Flow Cell](image)

Figure 2.6. The Reactive compound flow cell

2.8.5 The Windowless Cell.

This cell was developed for two reasons. Firstly, and more importantly, to measure cross sections at energies which are higher than the 11.3 eV cut-off of lithium fluoride windows (the windowless design allows spectra to be measured down to 30nm (41eV)). Secondly, such a cell eliminates the problems associated with the condensation or sublimation of compounds on the windows, a process which invalidates data acquired as it is unquantifiable.
The cell consists of two main components. The gas flow region; which consists of the aforementioned six way cross with associated injection system and exhaust, and a means of focussing light onto the gas flow region.

The monochromator operates at pressures many orders of magnitude lower than that of the gas flow region. As there is no physical barrier between the gas flow region and the low pressure components of the monochromator, a means of preventing back streaming of gas into the monochromator area was needed. This was achieved by using a differentially pumped glass capillary. The capillary had a narrow bore and therefore allowed only small volumes of gas to pass through it, whilst total internal reflection allowed the transmission of light without the light having to pass through any material which may cause attenuation. The actual system relies upon the capillary being mounted in such a way that one end is in the high vacuum region of the monochromator, the other end being in the centre of a large vacuum chamber, any gas entering the chamber from the flow cell expanding rapidly and being pumped away. The combination of the length and small bore of the capillary means that only small quantities of gas flow down the capillary, even though the pressure at the other end is considerably lower. During operation of the windowless cell, there is a free, reflective path between the source of the synchrotron light and the sodium salicilate coated window. Any absorption that may take place is due solely to the sample gas and background pressure gas, the absorption by the latter being so small as to be negligible.

A schematic diagram of the system is shown in figure2.7 and plate 2.4 below.
Key

LFP: Pneumatic LiF valve. Shuts automatically if P1 detects overpressure

P1, P2: Penning Gauges

XY: XY translator stage for capillary

C: Quartz capillary tube

T: Position of rear mounted chamber turbo pump

B: Baratron

OLV: Open LiF valve

PMT: Photomultiplier tube

Figure 2.7 The windowless gas flow cell.
Operation is similar to that of the windowed gas flow cell, the only main difference being the steering of monochromator light through the interaction region and onto the sodium salicylate window. Light is steered by adjusting the angle of the capillary light guide. This is done by means of two mutually orthogonal micrometer screws, attached to the capillary mount via bellows, allowing adjustment under high vacuum.

During the steering procedure, the light is seen by the naked eye as a small blue-green spot on the sodium salicylate window. A lack of light or a lens flare effect (one or more partial or full concentric bright rings of light) without bright central spot indicates incorrect alignment.

The windowless system does, however present problems regarding the determination of absolute cross sections, as the path length, \( l \), of the synchrotron light beam through the gas is not easy to quantify (a pressure gradient of sample gas exists in the capillary tube - the path length cannot simply be defined as the distance between the chamber end of the capillary tube and the sodium salicylate window). It is however possible, to calculate an effective path length by the measurement of \( \ln I_0/I_i \) as a function of pressure, and therefore number density \( n \), using a compound at a wavelength where the absolute cross section is known (Gingell J. M, 1999). A plot of \( \ln I_0/I_i \) against pressure yields a straight line, whose gradient represents the effective path length.
2.9 The Molecular Science Absorption Apparatus Electronics and Data Acquisition System.

The beam line electronics fall into two categories. Those that supply power to transducers, and those that process transducer outputs, to create useful signals. In some cases, both types of electronics are integrated into a single unit, for example within a Baratron pressure gauge.

With regards to data collection, there are four important parameters that are recorded during scans. These are cell pressure, intensity of light transmitted through the cell, wavelength and beam current. The intensity of light entering the cell is proportional to the beam current, and as the beam current slowly drops with time, a record of it is required to properly normalise photoabsorption data. Cell gas pressures should remain constant, although it rarely does so. For this reason, as for ring current, cell pressure is continuously recorded during scans. As the wavelength of light incident on the cell changes, so does the absorption of the light. Each apparatus has a unique (smooth) spectral profile (intensity versus wavelength) within its scanning wavelength range. This arises from synchrotron output characteristics and from varying reflective and transmissive properties of beam line components, such as windows and mirrors. This profile will change slightly with time, as synchrotron light intensity decreases. For this reason, during scans, pairs of scans are taken, with and without gas present in the cell. Scans with no gas present are termed "blanks", and those with gas present are termed "signal" runs. Photoabsorption spectra can then be obtained by comparison of blank and signal pairs.

Sensors for ring current, intensity and pressure have continuous analogue outputs. The monochromator wavelength is controlled by a stepper motor, setting a new monochromator position every second. Each time a new monochromator position is reached, the three analogue outputs of the transducers are read by the electronics and are converted by an analogue-to-digital converter into digital signals. Monochromator stepping and reading of the analogue voltages is synchronised using a crystal timebase. A digital signal, containing information on monochromator position, and hence
monochromator output wavelength is supplied, along with the three other signals, to the beam line computer, for processing and storage.

**Pressure**

This is monitored using an MKS Baratron gauge in which the pressure is measured by monitoring the electrical capacitance for various positions of a diaphragm. The diaphragm has the gas pressure to be measured on one side, and a reference sealed vacuum on the other. Variations of pressure cause the diaphragm to move and therefore change the capacitance, which is read by an electronic circuit that changes capacitance to an output voltage. The gauge therefore outputs voltage as a function of pressure. This is a continuous analogue output, that is read by the data acquisition electronics every time a new monochromator setting is reached.

**Ring current.**

The main synchrotron control room contains beamline current monitors. These output a voltage proportional to beam current, to the various beam lines. At Station 3.1 this voltage is monitored and recorded for each new monochromator position.

**Photomultiplier tube output.**

The photomultiplier tube operates from a continuous high voltage (-820V) supply and operates continuously during the run. The output current from the tube is passed into a current to voltage converter (Keithley 610c), from where a voltage signal proportional to the current is sent to the electronics.

**Wavelength.**

This is determined by the stepper motor position. The relation between wavelength and motor position allows the computer to store information on wavelength, when supplied with motor position information.

A block diagram for the data acquisition electronics is shown in figure2.8 below.
2.10 Acquisition of Cross Section Data.

Photoabsorption cross sections are measured as follows. A plot of intensity versus wavelength is acquired for an empty cell, known as a blank run. Gas is then admitted into the cell and another plot acquired for the same wavelength range, a signal run. The ring current, and hence intensity of light, drops slowly. This means that for any given gas under test, it is best to take blank and signal runs as pairs, with little delay between the two. A blank run will yield a continuum, as seen by the solid line in the hypothetical spectrum in figure 2.9. A signal run, will, however have an overall shape similar to the blank run, but will have superimposed troughs corresponding to areas of absorption, as seen by the dashed line in figure 2.9. Cases where the troughs reach the x axis indicate saturation, a condition which can be avoided by reducing path length, or more practically, the gas pressure.

Although a rough idea of the areas of absorption could be gained from only a signal run, the blank data is essential to normalize the data. This is done using a program that calculates an absorption cross section from the blank and signal spectra data.
The resolution of the spectra obtained is affected by several factors. Mechanically, the number of steps taken by the stepper motor between each measurement and the size of each step will affect the resolution, as this will determine the wavelength increment between each subsequent set of readings. The size of each step is a constant for the motor, but the number can be varied, such that the wavelength resolution can be varied from 0.01 nm to 10 nm. Another factor is the slit width, as this determines the angle subtending a range of grating wavelengths, such that the smaller the slit width, the smaller the angle, and so the higher the resolution. The cost of better resolution is a lower intensity, as less light is able to pass through narrower slits. The number of lines per unit length on the grating also affects resolution, the more lines the better the resolution, however the intensity per wavelength increment decreases as line density increases.

2.11 The Line Saturation Effect.

It is impossible to create light of zero bandwidth, ie of infinite energy resolution, and this may lead to errors when the Beer-Lambert law is used to calculate cross sections from the photoabsorption spectra. The line saturation effect results in errors of the measured spectral peak heights, and therefore the area under the peaks will also be determined incorrectly. Line saturation effects start to have a profound effect when the bandwidth of the spectrometer is similar or greater than the natural linewidth of the transition being studied. This is shown diagrammatically in figure 2.10 below (Gingell J. M, PhD 1998).
Spectrometer sampling bandwidth

Spectral line

Natural linewidth < bandwidth
gives poor cross section value

Natural linewidth > bandwidth
gives good cross section value

Figure 2.10 Representation of spectrometer bandwidth in relation to natural linewidth.

When the bandwidth of the spectrometer is greater than the natural linewidth, the logarithmic transform of the Beer Lambert law will result in the photoabsorption cross section having a weighted average, that in many cases will be significantly lower than the actual cross section. If, however, the spectrometer has a bandwidth less than the natural linewidth, the Beer Lambert law should give an accurate value for the absolute cross section. Spectral regions that have sharp structure are therefore the most affected by the line saturation effect, and for this reason when carrying out pressure calibrations (requiring good absolute cross sections, as opposed to accurate wavelength standards), oxygen is often used as it has a smooth continuum feature, the Schuman Runge band. Line saturation is an effect that varies with pressure, and so can be observed by varying the sample pressure. Line saturation is greatest at high pressures and results in a reduction in measured peak intensity and hence recorded cross section. The experimental solution for avoiding line saturation is to reduce sample pressure until a cross section value is obtained that is independent of pressure.

2.12 Calibration Using Reference Molecules with Well Known Spectral Features.

Wavelength Calibration.

To ensure the accuracy of measured data, it is imperative that prior to taking data on compounds whose spectra are unknown, the instrument is calibrated against well known data. In molecular spectroscopy, the most important calibration is that of
wavelength. Wavelength calibrations were therefore achieved by recording spectra for well known compounds.

**Nitric Oxide Calibrant.**

Nitric oxide is the preferred wavelength calibrant as it is stable and easy to handle, being a pressurised gas, and has well known spectral features between 5eV and its first ionisation energy at 9.27 eV. In order to calibrate the Daresbury Laboratory Molecular Sciences Absorption Apparatus, DLMSAA, the positions of peaks in the acquired absorption spectrum were compared to ones in the available literature, so that the energy scale could be accurately calibrated.

The nitrous oxide photoabsorption spectrum was recorded in 1 Å steps between 5.3 eV and 10.1 eV. The transitions arise from excitation of electrons in the ground state to both valence and Rydberg states. The photoabsorption spectrum for NO recorded on the DLMSAA is shown in figure 2.11 below.

![Photoabsorption spectrum of NO](image)

Figure 2.11. Photoabsorption spectrum of NO.

The positions of the observed peaks were then compared to the known energies, obtained from the literature, shown in table 2.3 below, and the DLMSAA calibrated accordingly.
<table>
<thead>
<tr>
<th>Peak</th>
<th>Upper State</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>((A^2\Sigma)^3s\sigma, \nu=0)</td>
<td>5.481</td>
</tr>
<tr>
<td>2</td>
<td>((A^2\Sigma)^3s\sigma, \nu=1)</td>
<td>5.771</td>
</tr>
<tr>
<td>3</td>
<td>((A^2\Sigma)^3s\sigma, \nu=2)</td>
<td>6.057</td>
</tr>
<tr>
<td>4</td>
<td>((A^2\Sigma)^3s\sigma, \nu=3)</td>
<td>6.340</td>
</tr>
<tr>
<td>5</td>
<td>((C^2\Pi)^3p\pi, \nu=0)</td>
<td>6.494</td>
</tr>
<tr>
<td>6</td>
<td>((D^2\Sigma)^3p\sigma, \nu=0)</td>
<td>6.608</td>
</tr>
<tr>
<td>7</td>
<td>((C^2\Pi)^3p\pi, \nu=1)</td>
<td>6.782</td>
</tr>
<tr>
<td>8</td>
<td>((D^2\Sigma)^3p\sigma, \nu=1)</td>
<td>6.891</td>
</tr>
<tr>
<td>9</td>
<td>((C^2\Pi)^3p\pi, \nu=2)</td>
<td>7.063</td>
</tr>
<tr>
<td>10</td>
<td>((D^2\Sigma)^3p\sigma, \nu=2)</td>
<td>7.168</td>
</tr>
<tr>
<td>11</td>
<td>((D^2\Sigma)^3p\sigma, \nu=3)</td>
<td>7.438</td>
</tr>
<tr>
<td>12</td>
<td>((F^2\Delta)^3d\delta, \nu=0)</td>
<td>7.690</td>
</tr>
<tr>
<td>13</td>
<td>((F^2\Delta)^3d\delta, \nu=1)</td>
<td>7.980</td>
</tr>
<tr>
<td>14</td>
<td>((H^2\Pi)^3d\pi, \nu=1)</td>
<td>8.120</td>
</tr>
<tr>
<td>15</td>
<td>(4p\pi, \nu=2)</td>
<td>8.530</td>
</tr>
<tr>
<td>16</td>
<td>(4p\sigma, \nu=2)</td>
<td>8.580</td>
</tr>
</tbody>
</table>

Table 2.3. Energies of assigned prominent spectral features of the NO photoabsorption spectrum.

**Pressure Calibration.**

As line saturation is an effect that is pressure dependent, and has the greatest effect on sharp peaks, pressure calibration is best carried out using a spectral feature that is broad and featureless. The oxygen molecule exhibits such a feature, known as the Schuman Runge band, in the energy region between about 7 and 9 eV, with a broad peak between 8.5 and 9.0 eV. Apparatus pressure calibration is carried out by recording a photoabsorption cross section for oxygen at an energy around the top of the peak, and then comparing it to previously recorded and trusted oxygen data. Discrepancies can then be used to create a normalization constant, that is subsequently applied as a divisor to cross section data recorded using the apparatus.
for other molecules. For example, if the cross section was 0.95 of that expected, cross section data would then be multiplied by the reciprocal of 0.95 to normalize the data.

A photoabsorption spectrum of oxygen, recorded on the DLMSAA, is shown in figure 2.12 below.

![Photoabsorption Spectrum of Oxygen](image)

Figure 2.12. A VUV photoabsorption spectrum of oxygen, recorded using the DLMSAA. The broad featureless band between 7 and 9 eV is the Schumann Runge band, used for pressure calibration.

The error on the cross section ($\sigma$) measured using the DLMSAA is given by:

$$\left(\frac{\Delta \sigma}{\sigma}\right)^2 = \left[\frac{(\Delta p)^2}{p^2} + \frac{1}{\ln(I_o/I)} \cdot \frac{1}{I_o} \cdot \left(\frac{\Delta[I_o/I]}{I_o}\right)^2\right]^\frac{1}{2}$$

(2.5)

$p$ being the sample pressure, $I_o$ the intensity of light transmitted through the empty cell and $I$ the intensity transmitted by a gas filled cell. Errors were found to be in the region of ± 10%, with an increase in the error for low absorption bands, and low sample pressures.
2.13 Spectra of Known Common Contaminants.

It is often useful to have to hand spectra of molecules that are known, or suspected to be contaminants in any synthesised sample. Common contaminants in the work outlined in this thesis were acetone and the major air constituents. Acetone was present as it is used as a means of finding leaks and air constituents were inevitably occasionally present. If a spectrum showed signs of contamination, steps were taken to remove the contaminant, and repeat the measurement until contamination was no longer seen.

The spectra that are shown below are for contaminants that were present in the samples that were measured using the DLMSAA

**Acetone.**

Acetone is a widely used laboratory solvent, both as a cleaning agent, and as a means of vacuum leak detection as it is highly volatile.

The photoabsorption spectrum for acetone was recorded using 1 angstrom steps, over a range of 6-10.3 eV, after the apparatus had been calibrated using NO.

The photoabsorption spectrum for acetone vapour is shown in figure 2.13 below.

![Photoabsorption spectrum of acetone in the range 6-10.3 eV.](image)

Figure 2.13. Photoabsorption spectrum of acetone in the range 6-10.3 eV.
The peak at 8.08 eV, corresponding to the 4s state was used as a means of detecting the presence of acetone vapour in samples used.

The energies of several assigned states of acetone (Huebner R.H, 1973) are given in table 2.4 below.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Assignment</th>
<th>Energy / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$B\leftarrow^1A_1 \ (n \rightarrow \sigma^*) / 3\sigma$ Rydberg state</td>
<td>6.35</td>
</tr>
<tr>
<td>2</td>
<td>Vibration associated with $B\leftarrow^1A_1$</td>
<td>6.49</td>
</tr>
<tr>
<td>3</td>
<td>Vibration associated with $B\leftarrow^1A_1$</td>
<td>6.63</td>
</tr>
<tr>
<td>4</td>
<td>Vibration associated with $B\leftarrow^1A_1$</td>
<td>6.77</td>
</tr>
<tr>
<td>5</td>
<td>3p</td>
<td>7.39</td>
</tr>
<tr>
<td>6</td>
<td>3d</td>
<td>7.84</td>
</tr>
<tr>
<td>7</td>
<td>4s</td>
<td>8.09</td>
</tr>
<tr>
<td>8</td>
<td>4p</td>
<td>8.42</td>
</tr>
<tr>
<td>9</td>
<td>4d</td>
<td>8.68</td>
</tr>
<tr>
<td>10</td>
<td>5s</td>
<td>8.83</td>
</tr>
</tbody>
</table>

Table 2.4. Energies of assigned prominent spectral features of the acetone photoabsorption spectrum.

**Water.**

Water is sometimes present as a contaminant as it is a constituent of air an is often present on the inner surfaces of vacuum components that have not been under vacuum sufficiently long to remove traces of it.

A photoabsorption spectrum of water is shown in figure 2.14 below.
Figure 2.14. The photoabsorption spectrum of water.

Nitrogen.
As nitrogen is the main constituent of air, it is important to know the absorption spectrum. Nitrogen has a very low cross section below 12 eV and therefore is not of importance to most photoabsorption experiments carried out for this thesis, as the energy cut-off is below 12 eV. A differential oscillator strength spectrum of nitrogen is shown in figure 2.15 below.
Figure 2.15 The differential oscillator strength spectrum of nitrogen (Jones N.C, PhD 2000).

The $a^1\pi_g$ state that is responsible for the structure seen below 11 eV is not optically allowed and therefore is not seen in photoabsorption spectra. For synchrotron studies, the structure above 12 eV is important as it contains structure that can be used to identify presence of nitrogen as a contaminant.


The UCL electron energy loss (EEL) spectrometer (Gingell J. M, PhD 1998) is a device that fires electrons of narrowly defined energy at a low pressure gaseous target, and measures the energy of scattered electrons. For a low scattering angle and high incident beam energy, the results can be compared to those of photoabsorption, as the cross section is proportional to the cube of the energy loss. Measurements of acetone taken using this spectrometer agree well with those of the synchrotron.

An EEL spectrum is shown in figure 2.16 below.
This is a raw EEL spectrum, it can be converted to a differential oscillator strength spectrum, using equation 2.6 (Huebner R.H, 1973) thus creating a spectrum that can be easily compared to a photoabsorption spectrum.

\[
df/dE \propto E \Delta \theta / R \left[ 1 / \ln(1 + (\Delta \theta / \gamma)^2) \right] I(E) \tag{2.6}
\]

where \( \gamma^2 = E^2 / 4T(T-E) \)

\( df/dE \) is the differential oscillator strength, \( T \) the energy of the incident electron, \( E \) the energy loss, \( \Delta \theta \) the acceptance angle, \( R \) the Rydberg constant and \( I(E) \) the intensity of the scattered electron beam.

The structured band between 6 and 7 eV corresponds well with that seen in the photoabsorption spectrum, and has been ascribed to a 3s Rydberg state, with the peaks at 8.08 eV and 8.84 eV being 4s and 5s states of the same series. In fact, all the structures below the first ionisation energy of 9.705 eV have been assigned to Rydberg (Huebner
R.H, 1973) states. The structure of the 3s Rydberg state at 6.35 eV and the peak at 8.08 eV corresponding to the 4s state are used to identify acetone as a contaminant. The EEL spectrum corresponds well with the photoabsorption spectrum.

2.15 Conclusion.

This chapter outlines the development of an apparatus for the measurement of the cross section of various important atmospheric and interstellar molecules. The work carried out using the Nd-YAG pulsed laser will be described in Chapter 3, and results obtained from the measurements taken at the Daresbury Laboratory will be discussed in Chapter 4.
CHAPTER THREE

OBSERVATION OF RESONANCE ENHANCED MULTI-PHOTON IONISATION USING A TUNEABLE LASER SOURCE

3.1 Introduction.

The secondary aim of this PhD was to devise an apparatus that can be used to study the spectroscopy of molecular fragments produced by electron impact dissociation. Although initially devised for the study of NO fragments, the ultimate aim is to upgrade the apparatus to allow the study of free radicals, such as CHx and CFx using Resonance Enhanced Multi Photon Ionisation, REMPI.

3.2 Advantages of Laser System.

A laser system is used as a light source as it provides access to high intensity light, which can be tuned with very high accuracy and precision. This allows ro-vibrational data to be obtained which would otherwise be inaccessible if other spectroscopic techniques such as Electron Energy Loss Spectroscopy or Synchrotron studies were to be employed. The reason the laser can provide such tunability lies in the fact that it uses a variable cavity dye lasing system (Moya Oscillator) which allows very narrow band tuning, where the wavelengths increments available are much smaller than those accessible by a synchrotron based system. The laser allows both REMPI and Laser Induced Fluorescence, LIF, processes to be studied.

REMPI is a process that involves the ionization of valence electrons by the transferal of the sum of the energies of two or more photons to the atom or molecule under study. In LIF processes the atom or molecule under investigation absorbs photon energy by stimulating an electron into a higher excited state, and then releases this energy. The
emitted wavelength is of equal or lower wavelength than the exciting photon, in the case of lower energy, the process may involve radiationless transfer.

3.3 Lasers. A Background and Theory.
Laser is the acronym for Light Amplification by the Stimulated Emission of Radiation. Laser light is unique in that it monochromatic, coherent, directional and of an intensity much higher than that achievable from conventional, or even natural light sources such as the Sun. It is these properties, and the ability to control the path of laser light with a much higher degree of accuracy than that of other light sources that has led to the development of many different applications of lasers, ranging from delicate medical and restoration applications, to industrial welding and cutting.

Monochromaticity.
Laser output is close to being fully monochromatic, that is of very nearly a single wavelength. This property is imposed by the emission process, which occurs when atoms in higher excited states fall to lower states, releasing the energy difference as light. Most of the light emitted in such a process occurs at a single wavelength, \( \lambda_0 \), however, some is also emitted at wavelengths slightly above and below \( \lambda_0 \). The wavelength spread around \( \lambda_0 \) is known as the line-width. A laser uses a resonant cavity, which is designed to only allow oscillations at certain discrete frequencies, known as axial modes, which substantially reduce the line-width, leading to near optimal monochromaticity. Axial modes are set up, because lasers induce resonance between a full and partial mirror, such that there are only a limited number of wavelengths whose integer multiples may fit exactly between the mirrors.

Coherence.
The laser is the only truly coherent light source available at present. Coherence is the degree of phase correlation that exists in the light radiation field in differing locations and times. Coherence is split into two categories. Temporal, the degree of monochromaticity of the light, and spatial, a measure of the degree of phase uniformity across the optical wave-front (a laser emits photons that are all essentially in phase). A coherent light source must comprise of a small radiating space, and the emitted light
must be of narrow bandwidth, with a wavelength spread equal to zero for an ideal system. Laser sources are close approximations to the ideal, with narrow band outputs and high degree of phase correlation. During the process of stimulated emission, the photons added to the stimulating radiation have a phase, polarization and energy, hence wavelength, identical to the light already present in the amplifying laser cavity, thereby effectively resulting in light amplification.

**Directionality.**
Laser radiation is highly collimated, with a low divergence. These properties allow laser radiation to be easily controlled, and focused onto small areas. An ideal laser emits a beam, which effectively consists of a uniform plane wave, such that the phase is constant along the beam profile, with only diffraction presenting a lower limit on the angular spread of the beam.

**Intensity.**
Lasers have the highest intensity of any artificial light sources available, and some are many orders of magnitude brighter than the Sun. Brightness is defined as power per steradian of solid angle per hertz of bandwidth. For a laser, the solid angle is the angle that the beam presents itself within as it leaves the laser aperture. As lasers are capable of providing high power levels within well-collimated beams, with very narrow bandwidths, their intensities are very high, with intensities as high as $10^{14}\text{Wm}^{-2}$ being available, compared to that of $1380\ \text{Wm}^{-2}$ for sunlight at the Earth's surface.

3.3.1 Theory of Laser Operation.
A material that has only two allowed energy levels will be explained. The Maxwellian – Boltzmann distribution function states that the number of particles, $N$, in a given energy state, $E$, in a material maintained at an absolute temperature $T$ is:

$$N=N_0\exp(-E/k_bT)$$  \hspace{1cm} (3.1)

$N_0$ being a constant for the material, and $k_b$ the Boltzmanns constant.

The numbers of atoms, $N_1, N_2$, in states $E_1, E_2$, are therefore related by:
\[ N_2 = N_1 \exp\left[-\frac{(E_2 - E_1)}{k_b T}\right] \] (3.2)

This is shown graphically in figure 3.1 below.

![Graph of the Maxwell-Boltzmann function showing how the number of atoms in an unperturbed two state system decays exponentially with increasing energy. The dashed line shows how population varies with energy, and has a negative slope.](image)

Figure 3.1. The Maxwell-Boltzmann function showing how the number of atoms in an unperturbed two state system decays exponentially with increasing energy. The dashed line shows how population varies with energy, and has a negative slope.

Whilst the material is maintained at thermal equilibrium, the two energy levels will be populated according to a dynamic equilibrium between the atoms. During a radiative process an atom can emit or absorb energy. A quantum of energy, equivalent to the energy difference between the two levels, is emitted when an atom decays from an energy level \( E_2 \) to \( E_1 \) in a process known as spontaneous emission. The converse is also possible, whereby an atom absorbs energy, in a process known as photon absorption. During absorption, an atom is excited to a higher level \( E_2 \) from its original level \( E_i \), the energy difference (gain) between the two levels corresponding to the energy of the exciting photon.

The photon energy for both cases is given by:

\[ h\nu_{21} = E_2 - E_1 \] (3.3)
When atoms in states $E_1$ and $E_2$ are exposed to a radiation field, of frequency $\nu_{21}$, then either the photons are absorbed by atoms in the $E_1$ state, exciting them to their $E_2$ states, or, ones in the $E_2$ states are stimulated to decay, with an associated photon emission of energy $h\nu_{21}$, in a process known as stimulated emission. During the absorption of light, the population of the upper level increases, although this perturbation away from equilibrium is usually small. This perturbation can be significantly increased, by means of the application of an intense "optical pumping" light source, such that the number density of $E_2$ states will increase, with a corresponding rate of decrease of the $E_1$ states, until a limit is reached when both states are equally populated.

This results in a population distribution roughly defined by:

$$N_1^* \approx N_2^* \approx (N_1 + N_2) / 2$$  \hspace{1cm} (3.4)

To understand the most basic mode of laser operation, a slightly more complex, three level material needs to be explained. This material has a third level, $E_3$, which is situated between levels $E_1$ and $E_2$. A three level system is depicted in figure 3.2 below.
Figure 3.2 A three level system. Optical pumping results in population equalization of levels $E_2$ and $E_1$, such that $E_2$ has a greater population than $E_3$. Note how the dashed line, that shows variation of population with energy, now has a positive slope.

Optical pumping has no effect on the population of state $E_3$, such that it remains at its equilibrium value, $N_3$, and the populations of the three states are $N_1^*$, $N_2^*$, and $N_3$ respectively. If photons of energy $h\nu_{23} = E_2 - E_3$ are present, they will induce transitions from $E_2$ to $E_3$ with associated stimulated emission, and will also be absorbed resulting in transitions from the $E_3$ to $E_2$ states. There are however more electrons in the upper state, $E_2$, as a result of the optical pumping, than in the lower $E_3$, and this results in an overall emission rather than absorption of photons of energy $h\nu_{23}$. A condition where there are more atoms in a higher level than a lower one, as is for the states $E_2$ and $E_3$, is known as a ‘population inversion’, and results in a system that is capable of amplifying the input light. The three level system can amplify light of frequency $\nu_{23}$, the signal frequency.

The population inversion principle is that which defines the operation of a laser. However, even though the output from such a system is coherent and monochromatic, it is of a rather low intensity. Intensity is increased by the use of a multi pass resonance cavity, within which the lasing medium is placed, in which the light oscillates, increasing in intensity with each pass. It is the feedback property of such a cavity that creates the intense output that is commonly associated with lasers. In order that a useful
output may be acquired from a laser system, the cavity is contained between two dielectric mirrors, one of which is partially transmissive, allowing loss (tapping off) of laser energy from the system. Stimulated emission that occurs along the axis between the two mirrors is reflected repeatedly, resulting in repeated stimulated emission within the lasing medium. Stimulated emission that occurs off axis is lost and dissipated in the surrounding media.

Laser resonances can occur in two different modes, those that are longitudinal, and those that are transverse. Longitudinal modes occur at different frequencies along the length of the laser cavity, within the gain bandwidth of the laser system. Transverse modes are seen as intensity variations in the cross sectional laser intensity profile, and are classified by the number of minima observed across the beam propagation front in two directions. The fundamental mode, where intensity is at a peak in the beam center, is known as the TEM_{00}.

A means of increasing laser power, for pulsed systems, is to employ Q switching. Q switching involves artificially preventing resonations in the laser cavity, resulting in very little or no feedback, resulting in no lasing. This allows the population inversion process to occur uninhibited, and to reach a maximum upper population density until lasing is required. When a high level of inversion is reached, the inhibiting system is removed, allowing lasing transitions to occur virtually simultaneously, resulting in a very short duration, extremely intense burst of laser light. The process derives its name from the fact that the efficiency of a resonant cavity is defined by its "Q" factor, namely that of its quality factor. A device that is often used for the purpose of Q switching is a Pockel's Cell. This consists of a crystal which becomes bi-refringent when an electric field is applied or removed, depending on the application. The magnitude of the change of birefringence is proportional to the applied voltage. The Q switch technique only works with polarized laser light, such that lasers that are not polarized are made to be by the addition of a quarter wave plate placed along the resonant path. The Pockel's cell works as follows: The applied voltage converts the device from a passive optic to a quarter wave plate, converting linearly polarized incident light to circularly polarized exiting light. The cavity mirror reflects the light, and in so doing reverses the direction of rotation so that when it passes back through the Pockel's cell, it emerges plane
polarized, but at right angles to its original plane of polarization, and is rejected by the polariser. This prevents resonance from occurring, thereby preventing further lasing action. Removal of the Pockel's voltage renders it a passive device, and allows resonant oscillations to occur. The ability to synchronise the Pockel's voltage with the laser pump source within the order of nanoseconds, allows for the creation of very high power, short duration laser pulses.

The laser output can be further increased by the addition of a second, non-resonant, laser amplifier cavity. The amplifier is a second piece of lasing material, which has undergone a population inversion due to optical pumping. Laser light passing through the amplifier stimulates the emission from the excited state, thereby increasing the optical power of the beam further.

3.3.2 Nd-YAG Lasers. Theory of Operation.

The source of energy for the three stage laser system used in this research was provided by an Nd-YAG laser. Nd-YAG lasers are used for a variety of industrial and medical applications, as the laser light they emit can be used as created, modified using non-linear optics, or used to pump further laser systems, giving access to a wide range of wavelengths. Neodymium is the active material, contained within a matrix, in the case of Nd-YAG, a Yttrium Aluminium Garnet (Y₃Al₅O₁₂) crystal, or in some cases, glass. The host material, acting as the matrix, is doped with Nd³⁺ ions. In the case of Nd-YAG lasing media, the doping process randomly replaces 1 - 2 % of the Y³⁺ ions by weight, with Nd³⁺ ions. It is the doping process that makes the transparent YAG material appear slightly mauve, as Nd³⁺ ions absorb in the red. Higher levels of doping are avoided, as the radius of Nd³⁺ ions is about 14% greater than that of the Y³⁺ ions, and increased doping levels would lead to stresses within the crystal, making it liable to crack or shatter when subjected to thermal stresses.

Excitation of the Nd³⁺ ions is by means of a broadband flashlamp. Only a relatively small proportion of the flash energy is used for excitation, as the neodymium ions absorption peaks between around 700 and 800nm, only absorbing a component of the white flashlamp output. The process of photon absorption results in transitions of the neodymium ions from their ground state to a higher energy level, from where they decay
to a metastable level, creating a population inversion between the $^4F_{3/2}$ and $^4I_{11/2}$ states, with stimulated decays to the lower state being responsible for the lasing. A simplified schematic for the transitions required for Nd-YAG lasing are shown in figure 3.3 below.

Figure 3.3 Energy level diagram for the operation of Nd-YAG electronic transitions leading to transitions that lase.

Nd-YAG is a four level system. The strongest emission is at 1064nm, although the splitting of energy levels by the Stark Effect results in weaker emissions at other wavelengths. The advantage with using a YAG crystal over that of using a cheaper glass matrix is that it has a higher thermal conductivity. The good conductivity results in laser beams which have good spatial and temporal characteristics. Nd-YAG lasers have been built with outputs in the order of tens of kW (continuous wave) and a few joules per pulse in pulsed operation, such as the system used in this research which has a maximum output of 2J at 10Hz and 6-9ns duration.
The laser used in this work employs the use of frequency doubling and mixing crystals. The crystals make mixing and doubling of laser radiation possible by a process where the incident alternating electric field of the laser light induces the transparent crystal medium to become electrically polarized, adding to the resultant radiation. At low intensities, the medium follows the incident light and therefore the polarization is at the same frequency as the incident light. At higher intensities, the polarization response is described mathematically as a power expansion of the inducing electric field. Mathematically, the square of a sine wave, \( \sin^2(\omega t) \), is given by \( \frac{1}{2}(1-\cos(2\omega t)) \), the second harmonic radiation generated is at a frequency twice that of the incident radiation, as governed by the polarization being dependent on the square of the incident field. A quantum mechanical approach describes this as the simple addition of two lower energy photons to create one higher energy photon, which is re-radiated. In a doubling process, the two original photons are of equal energy, and in a mixing process, they are of different energies. The energy of the resultant photon is always the sum of the energies of the two original photons. In media which are isotropic or have a symmetry center, so direction cannot be distinguished, this results in polarization which follows the direction of the incident field. Second harmonic generation in such media is not possible as the expression for the polarization dependence does not contain even powers. Crystals suitable for second harmonic generation need to be carefully grown so as to contain minimal defects, and need to be of types with no inversion centers, such as quartz, or \( \beta \)-barium borate (BBO).

3.4 The Design and Construction of the Continuum Nd-YAG Nanosecond Laser.

The laser system used was chosen as it gave access to finely tunable ultraviolet radiation and was known to be reliable. The main component is a "Continuum Powerlite 8000" Nd-YAG laser, which is self contained. This laser is used to optically pump a tunable dye laser. The output of the dye laser is then frequency doubled and mixed with the pump laser fundamental. The system is modular, being made up of three separate units. These being the Nd-YAG pump laser housing and power supply, the dye laser and dye circulator and finally the mixing and doubling unit. Additionally, the dye laser module has a computer to operate the dye oscillator optics. The various components are
protected from damage that may occur in the event of incorrect operation of cooling systems or other essential functions. These will be discussed in the section on safety and interlocks. Details of the various wavelengths available from the laser system are given in table 3.1 below:

<table>
<thead>
<tr>
<th>Wavelength / nm</th>
<th>Pulse duration/ns and energy / mJ</th>
<th>Source</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1064</td>
<td>6 – 9 2000</td>
<td>Powerlite 6000 Nd-YAG Laser</td>
<td>source for IR doubling and third stage mixing</td>
</tr>
<tr>
<td>532</td>
<td>&lt;6 – 9 750</td>
<td>doubled 1064nm IR</td>
<td>energy source for dye laser</td>
</tr>
<tr>
<td></td>
<td>&lt;6 – 9 up to 200</td>
<td>ND 6000 Dye Laser</td>
<td>doubling in third stage</td>
</tr>
<tr>
<td></td>
<td>&lt;6 – 9 up to 5</td>
<td>Third stage Doubling Crystal</td>
<td>third stage mixing</td>
</tr>
<tr>
<td></td>
<td>&lt;6 – 9 up to 10</td>
<td>Third stage Mixing Crystal</td>
<td>REMPI + LIF studies.</td>
</tr>
</tbody>
</table>

Table 3.1 Characteristics of Laser System.

3.4.1 The Nd-YAG Pump Laser.

The Nd-YAG laser consists of two YAG rods. The first acts as an oscillator and is pumped by a single discharge lamp. The second acts as an amplifier, and is pumped by two discharge lamps. Both rods and lamp assemblies are water cooled to remove the high amounts of waste heat energy released during the discharge of the powerful lamps. The laser is of a sufficiently high power to need to be operated in pulses, rather than continuous wave operation. The normal flash rate is 10 Hz, with a pulse duration of between 6 and 9ns. The pulse power can be controlled by varying the time delay
between the firing of the oscillator lamp and the amplifier lamps. Maximum power is achieved when a wave packet is amplified over its whole duration period of around 9 ns in the amplifier rod.

The Nd-YAG flashlamp/rod enclosures are shown in plate 3.1 below:

Plate 3.1 Nd-YAG rod and flashlamp housings. Top unit amplifier, bottom oscillator.

The oscillator system is the fundamental component of the laser system. It consists of a flash lamp pumped Nd-YAG rod contained between a fully reflective and a partially reflective dielectric mirror. Lasing in the cavity is controlled by means of a Pockels Cell. This is a device containing a crystal which causes a quarter wave rotation of photons at 1064nm when a voltage of 3600v is applied across it, and no rotation when no voltage is applied. By use of a polariser and quarter wave plate, there is a means of controlling whether oscillation is allowed to occur by application of voltage to the Pockels Cell. When the Pockel’s Cell is off, the lasing cavity is said to be closed, as oscillations cannot occur. When it is on, lasing can occur, and so the cavity in this state is described as being open.

Cavity closed: The horizontally polarised light from the rod passes uninhibited through the horizontal polariser and is rotated through 45° on passing through the quarter wave plate. It then passes unaffected through the Pockels Cell, as the voltage is off, reflects from a dielectric mirror and makes a second unaffected pass through the Pockels Cell. It then passes through the quarter wave plate which rotates it through a further 45°,
creating vertically polarised light which is rejected by the horizontal polariser, inhibiting the oscillation process.

Cavity open: horizontally polarised light from the rod passes through the horizontal polariser. It then is rotated by 45° by the quarter wave plate, and a further 45° degrees by the switched on Pockels Cell, creating a vertically polarised beam. This is reflected by a dielectric mirror, and passes back through the Pockels Cell, rotating through a further 45°, and is rotated the same again by the quarter wave plate. The beam is now horizontally polarised, and can pass through the horizontal polariser unaffected, allowing oscillation to occur.

Use of the Pockel’s Cell to control lasing is shown in figure 3.4 below, and a photograph showing the Pockel’s Cell and associated optics is shown in plate 3.2 below.

PC  Pockels Cell
QP  Quarter wave plate
H  Horizontal polariser
M  Fully reflective dichroic mirror
PM  Partially reflective dichroic mirror
R  Nd-YAG rod

Figure 3.4 Schematic illustrating operation of the Pockel’s Cell in conjunction with oscillator cavity optics.
Plate 3.2 The Pockel’s Cell and associated optics.

Infra-red light, at a wavelength of 1064 nm, created by the Nd-YAG rods passes into a doubling crystal. The output of the crystal consists of doubled laser radiation, at 532nm, and the original fundamental at 1064nm. The two beams pass towards a dichroic beamsplitter, such that they are separated and the 1064nm beam reflected twice to present both beams to separate shutters, acting as beamdumps when closed. A schematic of the Nd-YAG laser optics is shown in figure 3.5 below. Photographs of the Nd-YAG laser and the Pockel’s Cell and second harmonic generator are shown in plates 3.3 and 3.4 below.
1. Rear mirror.  2. Pockel’s Cell.  3. Quarter wave plate.
10. Dichroic separation.

Figure 3.5. Schematic of the Nd-YAG laser optical layout.

Plate 3.3. Nd-YAG laser and enclosure with hinged lid.
Plate 3.4. View of Pockel’s Cell, second harmonic generator, and associated optics. Green light is the second harmonic, at 532 nm. Note the mauve illumination around the Pockel’s Cell. This is due to stray flashlamp light leaving via the Nd-YAG rod (Nd\(^{3+}\) ions absorb in the red, giving the usually clear YAG rods a light purple colour).

### 3.4.2 The Nd-YAG Pumped Dye Laser.

The two wavelengths, at 1064nm and 532 nm, then enter the second stage. The 1064nm passes through the second stage, only being operated on by a delay line (to allow for delay of dye light which has a long path length due to various optical elements) so as to reach third stage optics at same time as the dye light.

The dye laser unit contains three major elements: the Moya oscillator, a pre-amplifier cell and a final amplifier cell. The oscillator and pre-amp cells are rectangular, whilst the final amplifier is of a capillary design. All three cells are transversely pumped by the pump laser beam. The dye system contains three laser beam paths. That of the pump beam fundamental, at 1064 nm, simply passing through via a delay line, that of the pump beam at 532 nm and that of the dye beam.

The 532nm green light passes through beam splitters splitting it into three beams. The least intense passes onto the Moya Oscillator which is a device containing a dye cell within a variable length cavity, with a grating used as a rear full reflector, allowing
wavelength tuning. The grating used has 2400 lines/mm, and the linewidth for the dye laser is 0.08 cm\(^{-1}\) at 560nm.

The 532nm beam of slightly higher intensity passes onto the primary amplifier, and the 532nm beam of greatest intensity passes onto the final amplifier. The path lengths are carefully chosen to allow maximum efficiency laser pumping of the dye, and the internal optical element delay times cannot be modified easily (minor adjustments can be done to achieve optimum lasing conditions). A schematic of the dye laser optics is shown in figure 3.7 below. The oscillator and amplifier modules contain cuvettes, small precision fabricated dye solution flow cells through which dye solution is continuously pumped in a closed loop. This allows the dye to be changed in either of the oscillator or amplifier loops (they are hydraulically isolated from one another and in most cases, different dye concentrations are used in the oscillator and amplifier loops). The possibility of using different dyes allows for the operation of the system with different output wavelength ranges. The use of dyes in solution allows dye concentrations to be optimised to achieve optimal lasing, both in terms of intensity and uniformity of laser output profile. A uniform output profile is very important for maintaining correct operation of doubling and mixing stages. In the work detailed in this thesis, the dyes used were Rhodamine 590 and Rhodamine 610. The two dyes were used together, dissolved in methanol. The peak output power was 20mJ per pulse, with a useable wavelength range of 567-599nm within 10% of peak power, at a wavelength of 579nm. An intensity versus wavelength plot for a mixture of Rhodamine 590 and 610 in methanol is shown in figure 3.6 below. A schematic of the Dye Laser is shown in figure 3.7 below, and a photograph is shown in plate 3.5 below.
Fig 3.6. Dye laser power as a function of wavelength. The dashed line shows the reduction in power after using the new dye mixture for 3 days.
Figure 3.7 Dye Laser optics.
Operation of the Moya Oscillator.

The active component of the Moya Oscillator is a diffraction grating / turning mirror pair, used instead of the normal fully reflective mirror used in the rear, non beam exit part of laser cavities. Wavelength selection is achieved by rotating the turning mirror by means of an actuator arm (called the sine drive arm), attached to a translation stage moved by a stepper motor and lead screw, whose rotation axis is centered on the diffraction grating. At any given angle, the mirror reflects a single wavelength back at the angle it left the grating. For a given specific angle $B$ between grating and mirror, the turning mirror reflects light with wavelength $\lambda$ striking the grating at an angle of $A$ back onto the grating. The grating equation below relates the two angles:
\[
\sin B + \sin A = d m \lambda, \quad (3.5)
\]
where \(d\) is the groove spacing and \(m\) the diffraction order.

Using the definition given by:

\[
\sin B' = \frac{x}{L} \quad (3.6)
\]

where \(x\) is translation stage movement and \(L\) the length of the arm. The Moya Oscillator is factory aligned so that \(B = B'\) and \(\sin A\) is a constant, such that \(x/L\) in equation 3.6 above can be substituted with \(\sin B\), giving the arm-grating sine drive equation 3.7:

\[
\lambda = \frac{1}{d m L} x + \text{constant} \quad (3.7)
\]

As \(1/dmL\) is a constant, the sine drive converts linear stage translation movement into a linear wavelength change. Therefore, by turning the lead screw that moves the stage (by means of a computer controlled stepper motor), the wavelength can be changed in a linear fashion. The system is capable of self calibration. It does this by driving the stage until and slightly past a photodiode detector. At this point, the stage slowly reverses, until a slot on a disc mounted on the drive motor shaft is detected by another photodiode, and the motor stops. This is known as the zero reset position. The sine drive equation 3.7 above contains two constants, the slope and \(y\)-intercept constant, recorded in memory as the zero point motor position.

The slope of the sine drive equation, \(1/dmL\) is kept in memory by the laser control computer as the \(\text{Å}/\text{turn}\) parameter, such that a desired wavelength can be reached by the computer drive control once the sine drive arm is calibrated. The wavelength increment per rotation is around 6.25 \(\text{Å}/\text{turn}\), but this varies slightly with each system – the exact value is unique to each laser and is permanently set in the computer memory.

A diagram of the turning mirror, translation stage and sine drive arm is shown in figure 3.8 below.
3.4.3 The Third Stage Doubling and Mixing System.

In the third stage, optics operate using infra-red light from the Nd-YAG laser, at 1064nm mixing with yellow dye light 567-599 nm. The dye light enters the doubling crystal and is frequency doubled, to create tunable UV of the frequency range 283.5 - 299.5nm. This UV is then mixed with the YAG fundamental to create higher energy UV, and as the mixing process uses the tunable UV source, the mixed higher energy UV is also tunable, within the range 223.9 - 233.7nm. The laser aperture at the end of the third stage utilises a Pellin Bocca prism, which separates out the various wavelengths (some of which enter the prism coaxially). The exiting wavelengths consist of:

1. The YAG fundamental at 1064nm,
2. The YAG second harmonic at 532nm,
3. The dye laser output within range 567-599 nm when used with Rhodamine 590/610mix,
4. Doubled dye laser output within range range 283.5 - 299.5nm.
5. The mixed output of doubled dye and YAG fundamental within range 223.9 - 233.7nm. For the work being carried out, it is only the mixed output that is useful; the other outputs are dumped onto an iris. Note: The wavelengths available from the dye laser and the doubling and mixing optics will depend on the dye(s) in use. The ranges quoted above are for a mixture of Rhodamine 590 and 610.
Auto-Tracking.
This is the name given to the negative feedback process that maintains correct doubling and mixing crystal alignment during wavelength scanning. To allow doubling or mixing to occur, the relevant crystal must be phase matched with the incoming laser beams. A crystal is said to be phase matched at a given tuning wavelength when the doubled or mixed beam is centered on the crystal’s zero order, brightest, tuning maximum. Remaining centered on the crystal’s output maximum whilst scanning is known as auto-tracking. In the case of doubling, a single dye beam is frequency doubled along the major axis of the doubling crystal. In the case of mixing, the doubled beam is made to overlap the pump laser fundamental within a mixing crystal, both doubling and mixing crystals are mounded on rotatable stages which move during auto tracking to maintain correct phase matching. To compensate for beam drift during rotation, each stage contains a compensator crystal, which by means of direct gear coupling, moves in an equal and opposite direction to that of the crystal. Each stage is equipped with a diode tracking system. This consists of a beam splitter, attenuator optics, lens and dual diode detector. A small proportion of crystal output light is reflected by the beam splitter and passes onto attenuation prisms. It then passes through a partially UV transmissive filter which attenuates most unwanted light (various wavelengths present other than light relevant to that stage) as well as reducing UV intensity. Finally it passes through a cylindrical lens which focusses the beam into a line, which illuminates two photodiodes. The output of the photodiodes is proportional to the amount of light striking them. During tuning, the diode units are aligned to be equally illuminated when a zero order beam is present. This means that when the crystal is fully phase matched, both diodes receive equal beam intensity, and output equal voltages. As the dye laser tunes and changes wavelength, one side of the beam entering the diode units will start to darken as a band of destructive interference appears, resulting in a voltage differential between the two diode outputs. The tracking electronics use this differential to rotate the stage to eliminate the difference and maintain correct crystal position. A schematic of the third stage optics is shown in figure 3.9 below, and a photograph is shown in plate 3.6 below.
PR1: Polarisation and rotation prism assembly.  
DCC: Frequency doubling crystal.  
QCC: Quartz compensating crystal.  
IP1, IP2: IR turning prism.  
QW1: Quarter wave plate.  
Stages 1 and 2: Harmonic positioning stages.  
TP1: Glan-Taylor tracking prism.  
D1: Beam present detector.  
D2: Dual photodiode tracking detectors.  

DP1, DP2: Turning prisms.  
MCC: frequency mixing crystal.  
IM1, IM2 IR mirror.  
AP1: Aperture pinhole.  
BS1, BS2: Beam splitters.  
PB1 :Pellin-Broca prism.  
CL: Cylindrical lens.  
F: Filters

Figure 3.9 Optical layout of third stage doubling and mixing system.
Plate 3.6 The Doubling and Mixing optics. To the right is seen the dye laser module, and to the left the two tracking controllers.

3.5 Operating the Laser System.

3.5.1 Tuning the Laser System.

Tuning is a general term for any process that improves the optical performance or laser beam quality. This is usually achieved by adjusting the positions of optical elements or by changing the concentrations of dye solutions. Occasionally, discharge voltages of the flash lamps may be altered for optimal performance. The laser parameters that are of importance during tuning are power and beam profile. Power is measured using a calorific power meter, and the beam profile monitored with burn paper, which is used in preference to a CCD imaging system as the paper can be used in confined spaces. This is a process whereby de-sensitised (exposed) photographic paper is placed in the path of the laser beam, resulting in varying degrees of surface damage (burns). For high power beams, the uncoated side of the paper is exposed to the beam, so the paper acts as an attenuator. At high power attenuation is necessary as severe burns do not allow any
surface damage details to be seen. The shape of a burn, and its structure is indicative of the profile of the beam being observed. Burns can either be taken with a continuously running pulsed beam, with the paper passed swiftly through the beam, or by firing the laser in single shot mode. For continuous burns, information can be gathered as to any short period periodic fluctuations in beam profile that may be taking place.

It is also possible to monitor the position of the infrared beam when operating at low power with a fluorescent card, whose coating fluoresces in the presence of intense infrared light.

3.5.2 Tuning of the Nd-YAG Pump Laser.
The Nd-YAG laser normally only requires tuning during initial installation and after replacement of damaged optics, such as replacement of Nd-YAG rods (after replacement of flash lamps, self locating optical mounts eliminated the need for major re-tuning). The only other need for tuning arises when the unit has been out of use for a long time period, in which case tuning is a sensible precaution to take to avoid possible optical damage and to optimise power. Tuning the pump laser consists mainly of adjusting the beam height and position relative to the optics, maintaining a centralised beam throughout the optical path and checking for beam clipping. Other tuning involves adjusting the flash lamp voltage to obtain optimum power, although this is a non standard procedure, and the laser manufacturers, Continuum, should always be consulted prior to such adjustments being made, as each laser system is unique, and over voltage can cause serious system damage.

3.5.3 Tuning of the Dye Laser.
There are two main reasons for tuning the dye laser. Firstly it is necessary during initial installation or when an optic has been replaced. Secondly, more frequent tuning is required every time a new dye solution is used.

Tuning generally falls into three categories:
1. Full system mechanical tuning, such as needed after an optic change
2. Power tuning, as needed to optimise laser output power after a dye change
3. Beam profile tuning, also needed after a dye change.

Tuning is usually carried out in the order specified above, although very rough power tuning is sometimes necessary when the dye and optical components have been simultaneously changed, with a beam of reasonable power being needed to allow full system tuning to be carried out.

System tuning involves adjusting optics to steer the beam correctly through the various optics. This involves changing the focus as well as the position of the beam. The only place where the beam is focused to illuminate the target optics with a profile other than circular is on the cells containing dye solution, known as cuvettes. The beam is made divergent prior to striking these to maximise beam area, and thus maximise the volume of dye solution illuminated by the beam. Focusing is usually by means of a spherical and cylindrical lens pair, allowing the beam to become approximately rectangular in shape, with control over width and length of illuminated area.

On entering the dye laser module, the pump beam is split in two by a beam splitter, the weaker (reflection) being passed onto the oscillator cuvette via a neutral density filter. The lasing system is very much sequential, as is the tuning. For this reason, the transmitted (high intensity) beam at the beam splitter can be attenuated by a removable beam dump in front of the beam splitter, allowing easy observation of the oscillator beam path through the amplifier cells, without presence of high intensity amplifier pump light.

Once the oscillator pump beam has been tuned, the oscillator output beam is tuned by making sure it passes through the pre-amp and final amplifier at the correct height and position. The next stage requires the positioning of the pre-amplifier and final amplifier pump beam, this being carried out in a similar way. Once this tuning is complete, minor modifications may still be required when optimising beam power and profile, as described below.

Beam power optimization is achieved by the adjustment of dye concentration. The system has two separate closed loop dye solution circulators. One supplies the oscillator
cuvette (dye cell), the other supplies both primary and final amplifier cuvettes. Initially a dye solution is made with suitable concentrations of the two dyes in methanol. Dye solutions are solutions containing dye molecules that absorb pump laser light, and re-emit at a longer wavelength. Methanol is the preferred solvent as it reduces line broadening effects of dye molecules in solution. It has been found that optimal concentrations are considerably lower than that recommended by the manufacturer, and the reduction of the dye concentration has totally eliminated cuvette burning, which was a consistent problem when higher, recommended, dye concentrations were used. For the following procedure, dye beam power is monitored using a calorific power meter, placed at the exit port of the final amplifier cuvette. Having filled both dye reservoirs with dye solution of suitable concentration, the Moya Oscillator is moved to the peak of the dye(s) absorption curve, and all the cuvettes are optically pumped at maximum power. While monitoring power, a small quantity of dye concentrate is added to the oscillator reservoir and is allowed to mix thoroughly for a few minutes. This is repeated until no increase in power is seen. The laser is now optimised for power output.

The final tuning process takes place now, whereby beam profile is optimised by the addition of dye solution or solvent to the reservoirs. To determine what action may be necessary, a multi-shot burn is taken at the position of the power meter. The burn consists of a circular thermal discoloration of burn paper, usually with one side, left or right, considerably darker (more burned) than the other. If the right side is lighter, a small quantity of concentrate needs to be added to the amplifier reservoir, and repeated until burns are symmetrical. If the left side is lighter, methanol needs to be added to the amplifier reservoir, and a similar add and test procedure carried out until an optimal (even) burn profile is achieved. With experience, knowledge is gained of how much the concentration needs to be modified and whether burns, which are apparently asymmetrical due to incorrect dye concentrations are in fact the result of small cuvette misalignments. As a uniform beam profile is necessary for correct operation of third stage optics, especially that of the optical tracking system, it is often necessary to sacrifice some beam power, to achieve a better profile (during profile optimization procedures, the power often drops, as the beam is no longer power optimized). Small realignment of cuvettes will be described here as this type of alignment can only be done
after beam profile has been optimised - without an optimised beam, it is hard to see the effects which will be described below, that are indicative of badly aligned cuvettes.

Bad alignment causes caustics, rings of light offset from the main beam, to be seen when observing the beam on a card placed normal to the beam a distance away from the laser exit port. Caustics should be removed by rotating the final amplifier in either the vertical or horizontal plane. Horizontal caustics occur from incorrect horizontal alignment and vertical ones from incorrect vertical alignment. A combination of the two can be seen when alignment is incorrect in both the vertical and horizontal planes.

3.5.4 Tuning of the Doubling and Mixing stage.

Basic tuning involves similar procedures as for the previous laser units, whereby the optics are tuned to allow the laser beam to pass centrally through the optics. The tracking beam, described above, must also be aligned with the tracking system to allow for correct tracking. This involves altering the position of the tracking diodes such that when the crystals are properly aligned, equal signal is obtained from both diodes. Tracking works by maintaining the beam in an on-axis position for the crystals, as the beam position changes (due to the dye scanning) by means of detecting which side the beam is biasing towards, and correcting the crystals position, to return to optimal position.

3.6 The Safety Interlocks.

All three stages of the laser system and associated modules are fitted with safety interlocks to protect the operator from injury and the laser from optical and mechanical damage. The triggering of any interlock shuts down power to the main source of energy - the Nd-YAG laser. The main interlocks are series wired micro-switch pairs which are tripped should any of the laser covers be opened, although these can be mechanically overridden for tuning purposes. These interlocks are also series wired with interlocks on the laser laboratory door for additional safety. All the other interlocks are concerned with protecting the laser system rather than the operator in the event of a system unit failure. These are pressure (flow) sensors on the dye circulators and closed loop cooling water circulator, and temperature sensors on the Nd-YAG rod heads. These interlocks
prevent damage occurring from overheating or burning of cuvettes due to lack of dye solution. They do not, however, prevent damage occurring from the use of incorrect dye solution concentration.

**The Nd-YAG Pump Laser Head Interlocks.**
The pump laser can only operate if the laser head remains sufficiently cool, $T < 25^\circ\text{C}$. Cooling is by means of a closed loop water cooling group which transfers heat energy via a heat exchanger to an external cooling system. The laser coolant must be flowing sufficiently fast to prevent tripping out flow rate switches and be of a low enough temperature to prevent tripping out the thermal switches. Work on alignment can only be carried out once all interlocks are reset and do not risk being tripped out.

The laser system used in this research had a design fault with the cooling group for the Nd-Yag pump laser. The symptom is a black micro fibrous material building up, and causing a considerable decrease in YAG output, due to the attenuation of flashlamp light. The cause was originally thought to be an anaerobic algae. It has recently been shown that the material is in fact being sourced from the closed loop cooling group pump, and is a mixture of graphite and grease. Due to serious system damage resulting from a flood in the premises above the laser, the laser system was replaced and the new cooling system is now of a design that does not suffer from these problems.

**The Dye Laser Unit Interlocks.**
This component has one safety interlock that switches off the ND-YAG pump laser when the cover is opened. It can be overridden to allow tuning of optics. There are two other interlocks, that shut off the pump laser if either the dye is circulating too slowly, or dye circulator is not switched on. This is to prevent cuvette burn damage, which occurs if the dye is not flowing fast enough to prevent it heating up and burning inner cuvette surfaces.

**The Doubling and Mixing Unit Interlocks.**
As for the dye laser, this unit has an interlock that switches off the pump laser when the internal cover is opened. The interlock also has an override feature to allow tuning.
3.7 Measuring LIF and REMPI.

Cross sections for REMPI and LIF processes were measured using the apparatus described below. Two experimental chambers were built, which allowed the design of the second to be based on experience gained from using the first.

3.7.1 The Basic LIF / REMPI Chamber.

This was designed and built in order to study the basic processes that are fundamental to this research. Having found optimal conditions with the test chamber, a new chamber could be built. A diagram of the chamber is shown in figure 3.10 below.

![Side view of the basic REMPI / LIF test chamber.](image)

Figure 3.10. The basic REMPI / LIF test chamber.

The basic chamber consisted of a copper tube fitted with a flanged T junction, F. The largest dimension of the chamber lies along the pipe perpendicular to the T junction. The ends of this pipe are fitted UV transmissive lithium fluoride windows, W1 and W2, to allow the passage of laser light along the major axis of the chamber. These windows are bonded to the pipe at the Brewster angle, to minimise laser reflections. To minimize entry of light into the interaction region, the major axis is fitted with baffles, B (only two shown), with centrally drilled holes to allow the passage of laser light. The baffles are coated with light absorbing black Dag to minimise scattered light, which enters through the windows. Gas admission is via inlet and exhaust pipes, P1 and P2, which allow for gas flow and chamber purging.
The chamber is mounted on a “V” bench ensuring that its major (laser) axis is always parallel to the surface on which it is mounted. The use of modified hose clips in conjunction with a self-aligning “V” bench allow the chamber to be easily and accurately mounted. The base of the bench has the provision of mounting onto a standard optical table, making it possible to construct rigid assemblies of optical components relative to the mount and therefore to the chamber.

**Detectors.** The flange on the chamber allows detectors to be easily interchanged. The detectors that were used were a simple ion detector consisting of ion plates for REMPI studies, and an optical detector for LIF studies. The REMPI detector was mounted directly on the flange, whereas for LIF, the flange adaptor merely housed a Lithium Fluoride window, that allows the transmission of LIF light to an optical detector. The close tolerance of the bolt holes and use of seated neoprene “O” rings made precise alignment procedures unnecessary, as the system automatically aligned during tightening, as long as the rotational position was correctly set.

**REMPI Detector.** The REMPI detector consists of a flange, F, fitted with two copper ion detection plates, the detector, DP, and repeller, RP. The plates are connected with copper wire directly to two BNC feedthroughs, BNCA on the air side and BNCV on the vacuum side, such that one of the plates, RP, is electrically connected to the chamber, whilst the other is isolated and makes contact with the central, signal, pin of the BNC feedthrough. When a voltage is applied across the plates, ions experience an accelerating force in the applied electric field, and constitute a current that can be externally detected in the rest of the detection circuit, by means of a current to voltage converter.

A diagram of the simple plate ion detector is shown in figure 3.11 below.
Figure 3.11. Flange mounting for simple ion detector.

The data acquisition system for the simple ion detector consisted of a current to voltage converter (a Keithley 600B electrometer), whose output was connected to a chart recorder, via a boxcar averager. As the laser fires at ten Hz, which is greater than the response speed of the chart recorder, a boxcar averager was used, whose output changed every second. This output was an average of the last ten inputs, re-sampling and averaging every second.

A schematic of the electrical system is shown in figure 3.12 below.

Figure 3.12. Schematic of the electrical system.
**LIF Detector.** The flanged interchangeable component of the LIF detector was simply a UV transmissive lithium fluoride window. The window allowed the processing and measurement of photons leaving the interaction region. A direct measurement would count the intensity due to fluorescence and scattered laser light. For this reason, a simple monochromator was installed between the chamber window, and photomultiplier. Since no condenser optics were used, the available light was only a small proportion of that created through fluorescence. This is an issue that should be addressed in future LIF designs.

The data acquisition system was much the same as for the REMPI detector, except that the signal was sourced from a photomultiplier tube output, as opposed to a pair of ion plates. A schematic of the electrical system is shown in figure 3.13 below.

![Figure 3.13. Schematic of LIF electrical system.](image)

**Vacuum System.** The main component is a Leybold Turbotronic 151 turbomolecular drag pump, capable of attaining $10^{-11}$ mBar. The turbopump is backed by a rotary vacuum pump, which pumps down to $10^{-3}$ mBar. The chamber, however, has quarter inch vacuum hoses, and as such pressures below $10^{-6}$ are not possible due to very slow pumping speeds. The reason for not having wider hoses lies in the fact that the chamber was a modification to an existing piece of apparatus, and being a test chamber, did not
warrant the conversion to larger diameter pumping pipes. This was not a problem, as in practice pressures required were well within those attainable by the apparatus.

**Gas Inlet System.** Gas flow rate, and hence pressure, is regulated by means of a gas bottle regulator, needle valve and on/off valve. A pressure of around 1.7 Bars upstream of the needle valve allowed for easy control of the flow rate. The use of both valves meant that the gas supply could be switched off whilst maintaining the needle valve position. This was very useful, as adjusting the needle valve is a lengthy process if long-term pressure stability is required. The pressure repeatability of the system was fairly good, such that after a period of no use, with the on off valve shut, the originally set pressure was reached when the on off valve was re-opened, provided all other variables remained the same.

The cell is maintained as a flow cell by the continuous pumping of gas from its exhaust. This is done via a quarter inch hose, which leads to a turbo molecular drag pump via an adapter. The long thin hose leads to long pump down times due to a high resistance to gas flow within the thin pipe.

**Signals and Data Acquisition.** As described above, the data acquisition system for the prototype chamber was a chart recorder. Signal from the ion detector plates, or photomultiplier tube was passed into an amplifying current to voltage converter. From here it passed into a boxcar averager, which was triggered from the laser trigger output, (with a short delay applied to account for the time of flight of the ions when used for REMPI). The output of the boxcar averager was the average of ten voltages it had received in the last second (laser operates at ten Hertz, and the boxcar averages every ten data bins) and the output of the averager changes once a second - the output hangs at the previous voltage until the new average is different from the previous one, thereby necessitating a change in averaged output. A boxcar averager was used as the chart recorder, has a finite response time, and could not cope with a voltage which varies ten times a second. A diagram showing the time relation between the various signals present in figure 3.14 is shown below.
A superior data acquisition system was developed by Dr. Haibo Zhao which involved a commercial analogue to digital converter which fed data to an I/O port which was processed by a home written program "EasySpec" (written by Dr. Zhao), which converted I/O input into a graphical output. This system was very useful, however following an upgrade to Windows 95, the program had an operating error that proved very difficult to fix. This resulted in the design of an analogue to digital converter and using software to list incoming voltages as a function of time. This is a system that was developed for use on the new chamber, and is discussed in section 3.7 below.

3.7.2 Measuring LIF and REMPI Spectra.

It is the ability of the laser to scan through a chosen energy band that makes it so important for high resolution spectroscopic work. The application of this is described below. The Moya Oscillator within the dye laser stage is the only part of the laser system to be controlled by the PC. The other control systems are integrated into the laser power supply unit rack and peripheral devices associated with the third stage, such as the tracking control electronics. The Moya Oscillator, is, however fundamental to the creation of tunable UV. The PC controls a stepper motor that controls the position of the Moya Oscillator cavity. The Moya optics can be set to run through an automatic calibration sequence to eliminate wavelength shift errors arising from the drift of the
mechanical coupling between drive motor and Moya grating. It is capable of running a self-calibration test to recalibrate itself. The Moya oscillator system maintains a constant optical bench temperature of thirty-five degrees Celsius to remove errors in wavelength occurring from the contraction or expansion of optical components and mounts.

The architecture of the user interface software is menu based, allowing operating parameters to be modified with ease. These parameters include the dye in use, start and stop positions of scan, scan speed and various others such as a self-test and calibration option.

3.7.3 REMPI Studies using the Basic Chamber.

**Set Up Procedure.**

Following installation of the ion detector flange, the interaction region of the chamber was aligned with the laser beam using a line of sight method. The chamber contains internal perforated baffles, aligned in such a way that any laser light entering the chamber must pass through the interaction region if it is to leave from the opposite window, without having interacted with the walls of the chamber or its baffles. This makes alignment easy. A well aligned laser will be seen as a circular spot on a piece of paper as it leaves the chamber, white paper being used as it fluoresces blue in the UV laser light. Incorrect alignment shows up as a shadow (part of the expected circular profile being obscured by the obstacle in its path). The chamber is adjusted until light is seen to pass through the interaction region producing a circular spot.

Having aligned the chamber, the laser was allowed to run for some 30 minutes to reach a constant temperature. Gas was then introduced into the chamber. The detector electronics were switched on, and after allowing a little time to see if the pressure was starting to drift, the data run started. A wavelength scan was started by initialising the PC to start the scan and simultaneously marking the start position on the chart recorder. There was always a small synchronisation error between the laser scan start time and the indicated position on the chart recorder. However, this was insignificant as the scans were slow and took up to three hours, the wavelength error therefore being extremely small (time synchronisation error was in the order of one second). At the end of the scan, a mark was made on the chart to show the time of the end of the scan. A typical plot acquired using the chart recorder is shown in figure 3.15 below.
3.7.4 LIF Studies using the Basic Chamber.

Recording LIF measurements used the same procedure as for REMPI, except that a monochromator and photomultiplier tube were used to acquire signal. In the project basic experimentation went no further than to irradiate the NO at a known fluorescence active wavelength, (226.13nm) and to scan the monochromator manually until a signal peak was seen, indicating that the transmission wavelength corresponded to the fluorescence wavelength. The aim was to create a system capable of detecting NO by means of fluorescence, for biological studies, and not to achieve an LIF spectrum as a function of wavelength. Running a scan as a function of laser wavelength and monochromator position is not possible if the aim is to observe unknown fluorescence wavelengths, unless, for every single laser wavelength increment, the monochromator was scanned through its entire range, to find the peak. Details of the biological studies are given in chapter six.
3.8 The REMPI and Electron Impact Dissociation Apparatus.

3.8.1 Introduction.

The electron impact dissociation apparatus is an extension of the REMPI system, as having created a system capable of detecting REMPI ions, REMPI is to be used as a means of detecting fragments created in electron impact dissociation processes. The apparatus consists of an evacuated chamber into which a sample gas is injected and exposed to a laser pulse. The pulse causes the gas to ionise in a process known as Resonance Enhanced Multi-Photon Ionisation (REMPI). The cross section is dependent on whether the laser photon energy corresponds to the (multiphoton) ionisation energy of the gas at any given wavelength. At such energies, ionisation yields will be considerably greater. Relative ionisation is either measured directly, by measuring the current created when ions are attracted to a plate, or indirectly, when ions are accelerated by a high voltage to a channel electron multiplier surface, where an electron cascade is created from each impact of sufficient energy, resulting in a voltage spike at the channeltron output.

The REMPI system is designed to detect ions created during electron impact dissociation, created by means of a beam of electrons emitted from a simple electron gun mounted above the interaction region. A photo of the chamber is shown in plate 3.7 below.
3.8.2 Design of Vacuum Chamber and Associated Components.

The apparatus can be thought of as consisting of four separate, but interlinked, systems. These are:

1. **The Vacuum System.** This is based around an eight port vacuum chamber and pumping station. The largest dimension of the chamber is a tube parallel to the z-axis. This encompasses a feedthrough at the top, below which is mounted an assembly consisting of an electron gun and Faraday cup, such that the volume between them coincides with the laser beam path. At the lowest part of this tube there is a flange that allows direct connection to a Leybold Turbotronic pumping station, with no reduction in pumping cross section at the pump interface. This results in a fast pumping rate.

   The remaining six ports all lie in the xy plane. The laser beam enters and leaves the apparatus parallel to the x-axis. To achieve this, two UV transmissive lithium fluoride ports, mounted at the Brewster angle, are used, allowing the laser to enter via one and leave via the other. Allowing the beam to leave the chamber, rather than dissipating it on an internal beam dump allows for easy alignment of the beam. As commercial flanged lithium fluoride windows were not available, custom ones were designed which consisted of a neoprene rubber "O" ring compression mount to hold the window in a
mount, itself brazed at the Brewster angle onto a pipe, attached via a flange to the chamber. This design permits rotation of the Brewster window, and easy replacement in event of window damage. The design of the window mount has allowed suprisingly low pressures to be reached, of around $10^{-8}$ mBar.

Parallel to the $y$-axis there are two ports, the larger of which supports the ion detection optics, and the smaller mounts the pressure gauges, although in the future it is intended that this will be used for the mounting of a quadrupole mass spectrometer. The use of two pressure gauges, a Pirani and a Penning, allows for the measurement of pressure throughout the full range of possible pressures, from atmospheric through to the ultimate pressure, $10^{-9}$ mBar.

The last two ports are the smallest. One is a viewport, fitted with standard fused silica glass, and the other serves as a means of injecting gas into the interaction region. The viewport glass is UV absorbing, thus allowing safe viewing of the interaction region during operation of the laser. The gas injection port consists of flange from whose center is mounted a quarter inch pipe, with a removable needle.

2. **The Electron Gun.** The electron gun currently in use is of an extremely simple design but may be upgraded in the future. The main components are a commercially available tungsten filament and a single anode. The electron optics are shown in figure 3.16 and plate 3.8 below.
Figure 3.16 Electron optical bench mounted on flange.

Plate 3.8. The electron gun assembly.

The gun assembly is mounted on an electron optical bench, EOB, allowing for future addition of lenses. The electron optical bench is mounted onto the chamber flange plate, FP, via a hollow adaptor, A, which allows the bench to be mounted whilst giving access
to the feedthrough. On this same bench, but on the other side of the interaction region, a Faraday cup, FC, is mounted, allowing the divergence of the electron beam to be measured. The Faraday cup is composed of an inner solid metal cylinder, isolated from an outer cylinder by means of a hollow PTFE cylinder. The Faraday cup is mounted in such a way that it is aligned with the axis of the electron beam. By measuring the current on the inner cylinder and comparing it to that measured on the outer cylinder, the divergence of the beam can be assessed. For example, a high inner current, and low outer current, would indicate a highly collimated beam. For ease of assembly, the repeller plate, RP, for the REMPI ion detector is also mounted off the electron optical bench.

A diagram of the electrical system for the electron gun is shown in figure 3.17 below.

![Diagram of the electrical system for the electron gun.](image)

Figure 3.17. Electrical measurement system used with basic ion detection plates.

The center of the filament wire was set to a desired voltage by using balancing resistors, R, and a floating output power supply. This allowed the energy of the electrons to be set.
The electron impact dissociation system was not tested as there was not sufficient time in the course of this project due to serious laser damage caused by a water from a flood in the building above the laser laboratory. The results of a functionality test carried out on the gun are given in chapter 6.

3. The Ion Detection Optics. There were two means available for the detection of ions. These were a simple plate system, and a channeltron based detector. The plates were used when pressures higher than those that can be used with a channeltron were used, that is $5 \times 10^{-5}$ mBar and above. A channeltron will break down if used at higher pressures, resulting in permanent damage.

The plates are a very simple means of ion detection. A potential difference is applied across two plates, an attractor and repeller pair, resulting in a net electric field force on the charged particles, ions. For convenience, in practice, the attractor grid was used as a "plate" when used in simple mode, thereby requiring no mechanical alteration when switching from channeltron to plate detection. The direction of the field determines the direction of attraction and repulsion of a particle of given polarity. For convenience, the same plate (attractor/detector) is always used as a detector. This means that when the need arises to detect ions of a charge opposite to ones currently being measured, the polarity of the plates is reversed (the magnitude of the voltage may also need to be modified for optimum performance). This allows for the detection of positive as well as negative ions. When ionization occurs, the charged particles move in the direction of the plate whose polarity is opposite to that of themselves, and constitute a net current. It is this current that is then measured externally by means of a Kiethley electrometer, which makes up the rest of the current loop. This type of measurement indicates the presence of ions as a continuum of varying intensity.

The channeltron is a more advanced means of ion detection, and allows for the observation of individual ions. The channeltron based system still relies upon the repeller plate, $R$, to push ions towards the channeltron, but uses an attractive grid, $G$, to accelerate ions towards the channeltron mouth, $M$, such that incoming ions have sufficient energy to overcome the (low) work function of the channeltron coating, resulting in the ejection of an electron during impact. Each successful ion results in
electron release, which in turn creates a cascade effect, such that individual ions create easily detectable pulses at the channeltron tail, $T$, (output). The polarity of the attractor grid and the channeltron mouth can also be reversed, allowing for the detection of both positive and negative ions and electrons.

When detecting $\text{NO}^+$ ions, the repeller plate was maintained at around 150V, the grid in front of the channeltron at $-10\text{V}$, the mouth at $-50\text{V}$ and the tail at 2500V. The repeller plate and grid combination filters and extracts only positive particles. The grid to mouth potential accelerates particles towards the channeltron, and the large potential between the mouth and tail enhances the cascade effect.

A diagram of the channeltron based detector is shown in figure 3.18 and photograph in plate 3.9 below.

Figure 3.18 Channeltron ion detector.
4. The Gas Inlet Line

The gas inlet system used was similar to the one used in the prototype chamber, however it fed gas directly from the source into the chamber, without using a pump on the gas inlet line as a means of reducing the pressure of the gas injected. This resulted in a significant reduction of gas usage.

The gas inlet system consists of a regulated gas supply (from a lecture bottle cylinder) that is fed directly into the chamber interaction region by means of a hypodermic needle. This needle is mounted in a Teflon sleeve, allowing the length of its protrusion into the interaction region to be modified with relative ease.

3.8.3 The REMPI Electrical System and Data Acquisition Electronics.

The electrical system for the processing and recording of ionisation events can be configured in four different ways. These are:
1. Simple plate detector used with chart recorder.
2. Simple plate detector used with a PC.
3. Channeltron system used with chart recorder.
4. Channeltron system used with a PC.

3.8.4 The REMPI Simple Plate Detector System.

The measurement system was based around the two detector plates, in practice a repeller grid and attractor plate, their associated power supply and an electrometer. The plates were operated at 50V, such that one plate was held at earth voltage, and the other maintained at a negative voltage.

The data acquisition system changed considerably from the basic system used to assess whether a REMPI signal could be captured using a chart recorder. This early system suffered from earth loop problems, arising from neutral and earth connections within the chart recorder. The preliminary solution was to use an isolation transformer for the chart recorder, and to not use a boxcar averager, as it could not easily be floated. The system showed that REMPI signals could be recorded, but suffered two major problems, that of recorder jitter, due to the laser pulse, and that the chart recorder casing was live at the same voltage as the plates. For this reason, the plate threshold voltage at which the ion signal could be measured was determined. The voltage was found to be around 10V, considerably lower than the previously used 150V. As the agreed limit for safe working voltage of exposed live components is 50V, that was the voltage chosen, being considerably higher than the threshold. The floating system is described here as it justifies the choice of the plate voltage, however, it is not shown diagrammatically as it was superceded by the use of a high pass filter, allowing isolation of the plate voltage (and earth loops), by means of a simple capacitor circuit.

Two differing types of data acquisition were tried. Chart recorder based, and PC based. In both cases the electronics remained the same, the only difference being whether a PC or chart recorder were used for data capture. Signal from the plates was fed into the electrometer, whose output was fed, via a high pass filter to the boxcar averager which was triggered by an attenuated laser pulse. The output of the boxcar was then fed either into the chart recorder or a PC. After several attempts with various software systems, a simple data logger was chosen. The system is based around a commercially available Motorola chip. This digitises eleven analogue inputs, multiplexes them and inputs them into the computer via the printer parallel port. Picolog software then processes and logs the inputs. For this experiment, only one input channel is needed, although in the future
the second channel may be used as a timebase. This could record time from start of the run by recording a voltage which slowly increased with time with regular incrementation. The chip powers itself from the 5V available at the printer port, and the only real consideration is the presence of any voltage differential between the computer ground and experiment ground. The voltage differential between the PC and apparatus ground was measured, as damagingly high voltages can exist in poorly earthed systems, capable of IO card or even motherboard damage. The voltage was measured to be a few mV, being low due to a spur earthing system connected to a "clean earth". A diagram of the data acquisition system is shown in figure 3.19 below.

![Diagram of the data acquisition system](image)

Figure 3.19. Simple plate REMPI data acquisition.

### 3.8.5 The REMPI Channeltron Based Detector.

The channeltron based detector is similar to the plate system, except that it relies on a different means of ion detection. Ions are repelled towards the attracting mouth of the channeltron, where a cascade effect creates a measurable signal at the at the channeltron tail. The channeltron based system uses three power supplies for interaction region ion repulsion / attraction, and one EHT supply for the channeltron tail, T. The power supplies are connected in a way that allows both negative and positive voltages to be created with respect to ground. Voltages stated are relative to ground. The first supply powers the repeller plate, R, and maintains it at 150V, to repel ions towards the attractor grid, G, which is maintained at -10V by the second power supply. The grid being 98% transparent allows most of the ions accelerated towards it to pass through uninhibited towards the channeltron mouth, M, maintained at -50V by the third power supply. As
the ions strike the low work function surface of the channeltron, they release electrons, which in turn cause an amplifying effect further down the channeltron. The cascade pulse effect causes a voltage peak to form at the tail of the channeltron, T, for each ion that enters the mouth. The voltage peaks created at the channeltron tail pass through a high pass filter, and into an amplifier. The amplifier inverts and amplifies the signal peaks and feeds them to a ratemeter. The ratemeter is a device that converts frequency (of incoming pulses) to a voltage. The full scale deflection of the device can be selected, to allow the measurement of a wide range of pulse frequencies. The voltage output from the ratemeter is fed directly into the chart recorder or PC. The PC based system is the same as that used for the basic ion plate detector. A diagram of the channeltron measurement and data acquisition system is shown in figure 3.20 below.

Figure 3.20. Electrical system for channeltron based detection and data acquisition.
3.8.6 Practicalities of Running the System.

All four detection systems are essentially very similar in operation, in that the gas flow to the chamber has to be stabilised, and then the laser scan parameters entered, with commencement of data logging when the laser starts a scan. Data logging is either started by marking a start point on the chart recorder and switching on the chart motor, or triggering the computer. The logging has to be synchronised with the start of the laser scan, else all the scan data will have a shift relative to laser wavelength. Small errors are inevitable, but as the time of a scan decreases, or the scan speed is increased, such errors become increasingly significant. An ideal system would consist of a system whereby the data logging computer and laser would both require a logic pulse to start operating. An external system, maybe something as simple as a manual source of a five volt trigger pulse, such as a push button switch connected to a five volt supply, would then trigger both laser and computer at the same time, eliminating wavelength (time) shift errors. A simple system could be devised and connected via the serial ports of both laser and logger computers, such that when the return key is pressed manually on one computer, the other one is also cued at the same time.

If the laser scan rate and data logging durations are set up correctly with respect to each other, the logging should stop at around the same time as the laser scan ends. The duration of a laser scan is determined by the wavelength range, the wavelength increment per step and the number of steps per second. These parameters are entered into the laser control computer, via a DOS based software interface. The maximum number of steps is ten, this being limited by the laser firing frequency of 10 Hz. The scanning system could scan at a greater rate, but this would be pointless, as this may result in the system taking no steps in the time between two consecutive laser shots. It is more efficient to achieve the same outcome by stepping at the same or lesser rate to the laser, and taking greater wavelength increments per step.

3.9 Ionisation Gauge Noise.

This is noise that is created by the ionization of sample gas by the ionization gauge.
It should be noted that this noise is similar in appearance to actual signal, and only becomes distinguishable as noise when a plot of signal versus wavelength is created. The amplitude is roughly one third that of real signal. This may seem rather high, but this is not noise in the conventional sense. It is undesirable signal from a localised source, which can be easily removed. Removal is either done by setting a virtual discrimination level once the data is being observed on a computer (by ignoring all signal below one third of maximum amplitude), or removed in practice by establishing a stable pressure, and then turning the ionisation gauge off. In practice, the noise is removed by switching off the ionization gauge. The pressure can, in such cases still be roughly monitored. This is because there is a gauge mounted between the needle valve and the needle injecting gas into the chamber. Once a steady flow rate is established, the relative chamber pressure can be measured on the gas inlet system gauge. If the chamber pressure rises, so does the pressure on this gauge, as resistance to flow at the location of the needle goes up, so the pressure in the gas supply line also rises. When a stable flow rate is established, the pressure in the line can be recorded, and monitored once the ionisation gauge is switched off. Any changes in chamber pressure will be mirrored by changes in the injection line pressure. This phenomenon has been tested to assess whether the relation between the two pressures is real, and results confirm that it is (at least when close to the measured ionisation gauge pressure - should the pressure drift excessively, the scan would be terminated, and the ionisation gauge switched on to assess the pressure conditions within the chamber).

3.10 Conclusion.
An experimental system has been developed to use laser radiation to probe molecular spectra and to detect molecular species. A preliminary chamber was successfully used to record a REMPI spectrum, and the design of the data acquisition system provided experience that was of use when designing and building the new refined chamber, which is now ready to be used in further research for the detection of ions created through electron impact dissociation processes. The electron gun and associated optics were shown to work, and these are currently being upgraded by two new students, Paulo Limao and Sam Eden. An LIF spectrum was also recorded, although this was of signal versus monochromator position, using a laser wavelength known to cause fluorescence. Due to a flood that caused
serious laser damage the results are limited to the demonstration of functionality and experimental setup.
CHAPTER FOUR

VUV PHOTOABSORPTION SPECTRA OF ATMOSPHERIC NITROUS OXIDES AND CHLORINE OXIDES

4.1 Introduction.
Over the past three decades environmental awareness and concern over the impact of human activities on the environment has increased significantly. The main areas of concern are those of global warming, caused by the release of so-called 'greenhouse gases', and damage to the ozone layer, caused by the release of ozone depleting molecules. The reactions involved in ozone depletion, although well known, form part of an overall mechanism that is not yet fully understood. NO plays a critical part in the chemical cycle of N$_2$O$_5$, OCIO and CIONO$_2$, which, amongst other species, play a critical role in the creation and destruction of ozone and other important compounds, such as nitric acid, (which is also a cause of acid rain). These molecules and their atmospheric reactions are discussed in their respective sections below.

4.2 Atmospheric Pollution Chemistry: Ozone and Related Molecules – An Overview.

Tropospheric Pollution and NO.
NO plays a key role in atmospheric chemistry as its concentration has a direct effect on the level of stratospheric and tropospheric ozone, leading to photochemical smog, and also it forms the precursor of nitric acid, a cause of acid rain. NO is created in the high temperature oxidation of nitrogen, in conditions such as internal combustion engines and lightning.

In the troposphere, ozone is an unwanted compound that is in equilibrium in photochemical reactions involving NO (released from vehicle engines) and sunlight in the daytime. The ozone itself, and reaction products of its reactions with unburned hydrocarbons in vehicle exhausts constitute the photochemical smog often seen around large cities on warm sunny days. The reactions are as follows: (B.J. Finlayson-Pitts, 1986; R.P. Wayne, 1988)
During the night, most of the NO is oxidised to NO\(_2\), resulting in very low levels of NO. The equilibrium is altered by catalytic reactions that either create or destroy ozone, according to ambient NO concentrations. In unpolluted air, CO is oxidised by OH, leaving an H radical, which reacts with oxygen to form a hydroperoxy radical, HO\(_2\) (B.J. Finlayson-Pitts, 1986)

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 & \text{(4.1)} \\
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} & \text{(4.2)} \\
\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M} & \text{(4.3)} \\
\end{align*}
\]

The behaviour of the hydroperoxy radical depends on the ambient concentration of NO (B.J. Finlayson-Pitts, 1986). At very low concentrations of NO, in the region of parts per trillion, as observed in remote areas, HO\(_2\) either reacts with more HO\(_2\), or reacts with ozone, reducing ambient ozone concentrations.

\[
\begin{align*}
\text{HO}_2 + \text{HO}_2 & \rightarrow \text{H}_2\text{O}_2 + 2\text{O}_2 & \text{(4.6)} \\
\text{Or} & \text{ } & \\
\text{HO}_2 + \text{O}_3 & \rightarrow \text{OH} + 2\text{O}_2 & \text{(4.7)}
\end{align*}
\]

However, in polluted areas, where NO concentrations are higher, HO\(_2\) reacts with NO to create NO\(_2\), recreating OH

\[
\begin{align*}
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2 & \text{(4.8)}
\end{align*}
\]

The NO\(_2\) photolyses by sunlight, equation 4.2 above, creating a free oxygen atom, that reacts with oxygen to form ozone, equation 4.3 above, so continuing the smog formation process.

Photochemical smog is also created by reactions of ozone with partially unburned hydrocarbons emitted from vehicle exhausts. The hydrocarbons, represented by R in
equations below, are oxidised following hydrogen subtraction to form peroxy radicals, which in turn oxidise NO to NO₂.

\[
\begin{align*}
\text{RH} + \text{OH} & \rightarrow \text{R} + \text{H}_2\text{O} \quad (4.9) \\
\text{R} + \text{O}_2 + \text{M} & \rightarrow \text{RO}_2 + \text{M} \quad (4.10) \\
\text{RO}_2 + \text{NO} & \rightarrow \text{RO} + \text{NO}_2 \quad (4.11)
\end{align*}
\]

The NO₂ is thus regenerated, and becomes available to create more ozone through reactions 4.2 and 4.3 as described above. The alkoxy radical, RO, is the chain carrier in the ozone creating chain reaction. It reacts with oxygen to create amongst other compounds the hydroperoxy radical, HO₂, NO₂ and OH, such that the cycle continues (R.P. Wayne, 1988) and (K.H.Becker, 1991).

Another even more noxious compound than ozone, peroxyacetyl nitrate (PAN), is a constituent of photochemical smog and is toxic to both plants and animals. The reactions are as follows: (R.P.Wayne, 1988).

\[
\begin{align*}
\text{RCO} + \text{O}_2 & \rightarrow \text{RCOO}_2 \quad (4.12) \\
\text{RCOO}_2 + \text{NO}_2 & \rightarrow \text{RCOO}_2\text{NO}_2 \text{ (PAN)} \quad (4.13)
\end{align*}
\]

The major final product of atmospheric NOₓ is nitric acid, formed in the following reaction:

\[
\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M} \quad (4.14)
\]

The nitric acid is removed from the atmosphere by precipitation, leading to acid rain, the cause of forest damage, and erosion of limestone city buildings (and natural rock formations).

4.3 Stratospheric Ozone – the Ozone Layer and Related Anthropogenically Affected Reactions.

Although unwanted in the troposphere, ozone is an important constituent of the stratosphere, where it absorbs the Sun’s harmful UV-B rays (less than 300nm) and prevents them reaching the Earth’s surface. A reduced ozone layer has led to a greater
intensity of damaging UV rays reaching the Earth's surface, and has led to an increase in skin cancer rates, damage to plants and a rapid expansion of phytoplankton. Stratospheric nitrogen oxides are involved in processes that deplete the ozone layer, and are associated with the increasing ozone hole over Antarctica.

The environmental damage has led to many new areas of research and to studies of compounds known to play key roles in atmospheric chemistry. Gaining a better understanding of the atmospheric processes of these compounds allows improved atmospheric models to be created, these models may then help us understand how to modify dangerous emissions and hence reduce their environmental impact. Ozone is, however, created naturally in the stratosphere, and exists in equilibrium according to the following equations of the Chapman cycle (S. Chapman, 1930):

\[
\begin{align*}
O_2 + hv & \rightarrow O + O \quad (4.15) \\
O + O_2 + M & \rightarrow O_3 + M \quad (4.16) \\
O_3 + hv & \rightarrow O_2 + O \\
O_3 + O & \rightarrow 2 O_2 \\
\end{align*}
\]

This simple equilibrium mechanism predicts an ozone concentration that is about twice that which is observed. The reason for the discrepancy is now known to be as a result of catalytic destruction of ozone by free radicals according to the following reactions:

\[
\begin{align*}
X + O_3 & \rightarrow XO + O_2 \quad (4.19) \\
XO + O & \rightarrow X + O_2 \\
Net: O_3 + O & \rightarrow 2 O_2 \\
\end{align*}
\]

X being a free radical of the hydrogen (HOx), nitrogen (NOx), chlorine (ClOx) or bromine (BrOx) families (B.Osborne, 2000).

The free radical, X, is one created by the photodissociation of various natural and man made compounds. The most significant compounds are man-made chlorofluorocarbons (CFCs), which have a lifetime of hundreds of years in the stratosphere and, as a result of their catalytic behaviour, each chlorine radical can destroy up to tens of thousands of ozone molecules.
When the photoactive compounds react with NO\textsubscript{2}, they form nitrates that are not photosensitive, and are therefore removed from the cycle:

\[ \text{ClO} + \text{NO}_2 + M \rightarrow \text{ClONO}_2 + M \quad (4.22) \]

However, these nitrates are re-generated into photosensitive compounds by reactions on the surfaces of ice particles in stratospheric clouds over Antarctica in winter. This results in the release of compounds that are photosensitive and photolyse easily, leading to the creation of compounds that destroy ozone.

\[ \text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3 \quad (4.23) \]
\[ \text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HNO}_3 \quad (4.24) \]

The nitric acid is removed by precipitation, causing acid rain, removing a possible source of NO\textsubscript{x}, which could lock the harmful ClO in the form of chlorine nitrate.

It is the importance of the free radical reactions that is the reason for needing more data on molecules that can form these radicals. In the work carried out for this thesis, the molecules that were studied were those that create the nitrogen and chlorine radicals, namely N\textsubscript{2}O\textsubscript{5}, Cl\textsubscript{2}O and ClONO\textsubscript{2}.

N\textsubscript{2}O\textsubscript{5} plays an important role in the atmosphere as a reservoir for NO\textsubscript{x}. In the troposphere it has been linked to the processes that create and destroy the NO\textsubscript{3} radical, and the temperature dependence of its decomposition (to NO\textsubscript{2} and NO\textsubscript{3}) is such that it can transport NO\textsubscript{x} from cold to warmer regions of the atmosphere. N\textsubscript{2}O\textsubscript{5} is easily converted into HNO\textsubscript{3}, in doing so creates a permanent sink of NO\textsubscript{x} as well as creating acid rain.

### 4.4 Photoabsorption Spectra of N\textsubscript{2}O\textsubscript{5}

N\textsubscript{2}O\textsubscript{5} plays an important role in stratospheric chemistry as it is involved in reactions involving compounds whose concentrations have a direct effect on ozone levels. N\textsubscript{2}O\textsubscript{5} is formed by the reaction of NO\textsubscript{2} with NO\textsubscript{3} (equation 4.27 below). NO\textsubscript{2} and NO\textsubscript{3} are both formed by ozone depleting reactions, were NO\textsubscript{x} compounds act as catalysts. NO is first
oxidised to NO₂ and further oxidised to NO₃ (equations 4.25 and 4.26 below). N₂O₅ reacts with water vapour to form nitric acid, a source of acid rain. The N₂O₅ also acts as a reservoir of active nitrogen, which becomes available for reaction when N₂O₅ photodissociates, releasing NOₓ which becomes available for further catalytic destruction of ozone according to equations 4.19, 4.20 and 4.21 above.

The N₂O₅ was synthesised on site and used shortly afterwards on the synchrotron beamline. The synthesis procedure is outlined below.

### 4.4.1 Synthesis of N₂O₅.

N₂O₅ is a compound that is highly reactive and unstable at room temperature, with a melting point of 293K. As a result, when samples of N₂O₅ are required, it is common practice to synthesise it locally, preferably in the laboratory where it is required. Although it is possible to substantially reduce the reactivity and unstable nature of the compound by storing it at liquid nitrogen temperature, 77K, in practice it is often simpler, and safer, to synthesise it on location.

N₂O₅ is synthesised by the reaction of NO and O₃ at room temperature. NO is a commonly available pressurised gas, supplied in cylinders. O₃ however, is even more unstable and reactive than N₂O₅ at room temperature. For this reason, it too is synthesised, and purified, in the laboratory where it is required.

The N₂O₅ used in the studies outlined in this thesis was synthesised in the UCL custom designed reaction apparatus. The apparatus, shown schematically in figure 4.1 below, consists of a network of glass pipes, valves and "Youngs" couplings connected to simple vacuum apparatus. The whole assembly is mounted on a single trolley, allowing easy transfer from the synthesis laboratory, to the experiment.

The entire apparatus is pumped out to remove traces of water. O₃ is synthesised in the apparatus by flowing oxygen from a cylinder, C₂, (BOC 99% pure) through a commercial discharge ozoniser, Fischer 502, at a rate of 100 l/hr, with a resulting yield of 5g O₃ per hour. The O₃/O₂ mix then passes through a drying trap ,T₂, suspended in an acetone/dry ice slush, at 195 K. At the same time, NO is passed from a cylinder, C₁,
through a similar drying trap, T1, also held at 195 K, and passes to a “T” junction, where it mixes with the O$_2$/O mixture, and where reactions take place that lead to the formation of N$_2$O$_5$.

The reactions are as follows: NO is first oxidised to form NO$_2$ and further oxidised to form NO$_3$, which reacts with the ambient NO$_2$ to form N$_2$O$_5$. Although NO and NO$_2$ are just as readily available, NO is used as it is easier to dry.

The reactions are shown in equations 4.25, 4.26 and 4.27 below.

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \quad (4.25) \\
\text{NO}_2 + \text{O}_3 & \rightarrow \text{NO}_3 + \text{O}_2 \quad (4.26) \\
\text{NO}_3 + \text{NO}_2 & \rightarrow \text{N}_2\text{O}_5 \quad (4.27)
\end{align*}
\]

The reactions are allowed to take place for approximately an hour, with taps A1 and A2 open, such that the flow is in direction A. The products flow through trap T3, into a removable trap mounted on RTC (removable trap coupling) maintained at 195K in an acetone/dry ice slush. Here the N$_2$O$_5$ condenses as a white crystalline solid, leaving the unsublimed gaseous products and reactants to be pumped away. After an hour, the NO flow is shut off, and valves A1 and A2 closed, and B1 and B2 opened. This now reverses the direction of the gas flow from the ozoniser, so that it now flows in direction B. The slush bath is removed from the removable trap at RTC and placed under trap T3. As the removable trap warms, the ozone flow carries with it previously formed N$_2$O$_5$ and any other NO$_x$ products, which react with the ozone in the transfer pipe and mixing bulb, MB, to form N$_2$O$_5$. On reaching the cooled trap, T3, any N$_2$O$_5$ present sublimes and is trapped, allowing unreacted NO$_x$ and O$_3$ to be pumped away. The process of transferring the solid from trap-to-trap is known as trap-to-trap distillation purification, and is repeated until any brown/yellow discolouration, NO, is no longer seen when the trap is cooled to 77K using liquid nitrogen. For convenience, the last distillation is usually into the removable trap, to allow easy transferral to the experimental area.

A schematic of the N$_2$O$_5$ synthesis apparatus is shown in figure 4.1 below:
Figure 4.1. Schematic of $\text{N}_2\text{O}_5$ flow apparatus.
4.4.2 Determination of Possible Sample Contamination.

Due to the synthesis method for N$_2$O$_5$, there was a possibility that the samples created were contaminated. The work carried out for this thesis covers an energy range that spans much further to higher energy than that of Yao et al (Yao F, 1982) which is used for the NASA recommendations. A spectrum showing the contamination, compared to a pure sample spectrum of N$_2$O$_5$ is shown in figure 4.2 below, along with a difference plot for the two spectra.

![Figure 4.2](image)

Figure 4.2. Our spectra showing effects of impurity. Squares show measured spectrum of impure N$_2$O$_5$. Free line indicates spectral contribution of the impurity. Circles indicate subtracted spectrum of N$_2$O$_5$.

There are discrepancies between this work and that of Yao et al, whose work forms the basis of NASA standards for N$_2$O$_5$ cross sections. Our data, as well as having cross sections that are around 40% greater, also have a different spectral profile to that of the NASA recommendations. A possible explanation is the contamination of the NASA sample with absorbing impurities, such as NO$_2$, N$_2$O$_4$ and HNO$_3$. It is thought that NO$_2$ did not constitute an impurity as it has an easily identifiable structured spectrum in the UV (Au JW, 1997). At the pressures used, the concentration of the dimer, N$_2$O$_4$, in equilibrium is significantly lower than that of NO$_2$, such that it is not expected that it contributed to the spectrum observed. As N$_2$O$_5$ is the anhydride of nitric acid, care had been taken to remove traces of water by flaming the apparatus prior to synthesis. However, there were no differences seen between spectra obtained with the use of nylon (known to remove nitric acid) as opposed to those that had not. This suggests that the
impurity was not nitric acid either. The spectrum of nitric acid is known (Suto M, 1984) and it shows a strong absorption peak at 190nm and only absorbs weakly at 160nm, a wavelength where the N₂O₅ absorbs the maximum. For these reasons, there is confidence in the idea that the spectra recorded did not have significant features or perturbations as a result of nitric acid contamination. However, the impurity was seen only after a sample of N₂O₅ was kept at 233K for several hours.

The justification for trusting our data as opposed to that of the NASA recommendations is that our data spans into energies high enough to show the shoulder, as seen in figure 4.2 above, and this makes the identification of contributions of impurities, by spectral comparisons to be easier as at higher energies the impurity spectra differ from that of N₂O₅.

4.4.3 Results.

After synthesis, the N₂O₅ was usually taken to the beamline in a trap, maintained at a safe temperature of 255K by a dry ice/acetone slush bath. Once the trap had been attached to the DLMSAA, it was maintained at a low temperature, and residual gas pumped away. The N₂O₅ was then allowed to warm to room temperature allowing some sample to sublime and enter the apparatus. The experimental cell, capped with LIF windows, was constructed of Pyrex to reduce the likelihood of N₂O₅ wall losses. For the same reason, N₂O₅ was continuously flowed through the cell (at pressures between 0.05 and 0.2 torr). The cell path length was 16 cm and the spectral spacings of the scans were between 0.05 and 1 nm. The scans were run in the usual way, at an ambient temperature of 295 ± 3K. As N₂O₅ is gaseous at room temperature and vacuum conditions, no problems of sublimation or condensation were encountered within the apparatus.

The photoabsorption spectrum of N₂O₅ has been studied at wavelengths above 200nm by Johnson et al (Johnston HS, 1974; Graham RA, 1975; Yao F, 1982) and also by Harwood et al (Harwood MH, 1993; Harwood MH, 1998). In this work, the measurements were extended into the vacuum ultra-violet (VUV) region, measurements being taken between 150 and 240nm.

For the Daresbury experiments, a signal from a strongly absorbing impurity was observed a period of a few hours after the runs started. It is known that N₂O₅ can form nitric acid in the presence of water, and so the experiments carried out using the
conventional spectrometer used N₂O₅ that had been passed over nylon, which is known to remove traces of nitric acid to see whether this would alter the absorption parameters. No effects resulting from nitric acid were found.

All the Daresbury spectra showed a broad peak with a maximum absorbance at 160nm. No evidence for fine structure was found, even when the highest resolution (0.05nm step size) scans were run. Spectra recorded at differing pressures were consistent with each other, although that measured at 0.2 torr did show signs of saturation at the absorption maximum. Absolute cross sections were calculated from the 0.2 torr data taken over a range of 190 – 240nm. The spectrum over this spectral range is shown in figure 4.3 below, and absolute cross sections are listed in 2nm intervals in table 4.1 below. The figure also shows, inset, data obtained using the conventional laboratory UV-Vis spectrometer.

Figure 4.3. The photoabsorption cross-section for N₂O₅ obtained using the Daresbury Synchrotron, and conventional laboratory UV-Vis spectrometer, inset.
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<td>22.5</td>
<td>226</td>
<td>0.97</td>
</tr>
<tr>
<td>182</td>
<td>20.7</td>
<td>228</td>
<td>0.86</td>
</tr>
<tr>
<td>184</td>
<td>19.2</td>
<td>230</td>
<td>0.79</td>
</tr>
<tr>
<td>186</td>
<td>17.7</td>
<td>232</td>
<td>0.72</td>
</tr>
<tr>
<td>188</td>
<td>16.4</td>
<td>234</td>
<td>0.66</td>
</tr>
<tr>
<td>190</td>
<td>14.9</td>
<td>236</td>
<td>0.63</td>
</tr>
<tr>
<td>192</td>
<td>13.8</td>
<td>238</td>
<td>0.61</td>
</tr>
<tr>
<td>194</td>
<td>12.5</td>
<td>240</td>
<td>0.56</td>
</tr>
<tr>
<td>196</td>
<td>11.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1. Photoabsorption cross sections for N$_2$O$_5$. (1 Mb = 10$^{-18}$ cm$^2$)

An experiment to determine pressure dependence was carried out at 160nm. The pressure rose as the sample was warmed from 195K and then cooled. Although the pressure dependence appears linear, it does show slight signs of hysteresis. The data is shown in figure 4.4a below.

A least squares fit gave a cross section value of 42.0 ± 1.5 Mb (95% confidence), compared with a value of 40.3 Mb given in table 4.1, from measurements taken at
constant pressure. The agreement between the two values is good, and although the statistical errors in the pressure plot are small, an overall error of 15% is assigned, to allow for possible systematic errors.

Further experiments carried out by B. Osborne et al (B.A. Osborne, 1998), using the conventional spectrometer between 200 and 240nm confirmed that absorbance varies linearly with pressure, as shown in figure 4.4b. below. The figure also shows that there was no significant difference in the spectra obtained using N$_2$O$_5$ that had been passed over nylon, as opposed to this that had not.

Cross sections calculated from the pressure plots are compared with the synchrotron data in figure 4.2 and are compared in table 4.2.

Figure 4.4. (a) Plot of absorbance vs pressure for $\lambda = 160$nm. Circles = sample being warmed, squares = sample being cooled. (b) Plots of absorbance vs pressure for $\lambda = 210$nm (squares), $\lambda = 220$nm (circles) and $\lambda = 240$nm (triangles). Open symbols for sample passed over nylon, filled symbols sample not passed over nylon.
Table 4.2. Comparison of photoabsorption cross-sections obtained using a synchrotron and a conventional spectrometer between the range of 210 and 240nm.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Cross-section (Mb)</th>
<th>Cross-section (Mb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conventional</td>
<td>Synchrotron</td>
</tr>
<tr>
<td>210</td>
<td>4.22 ± 0.24</td>
<td>4.19 ± 0.51</td>
</tr>
<tr>
<td>220</td>
<td>1.82 ± 0.07</td>
<td>1.55 ± 0.40</td>
</tr>
<tr>
<td>230</td>
<td>0.91 ± 0.02</td>
<td>0.79 ± 0.29</td>
</tr>
<tr>
<td>240</td>
<td>0.64 ± 0.02</td>
<td>0.56 ± 0.22</td>
</tr>
</tbody>
</table>

The pressure plots in figure 4.3b also show that the passage of $\text{N}_2\text{O}_5$ through nylon, to remove trace nitric acid contaminant, does not affect the spectrum recorded, indicating that nitric acid is not an important impurity. The values of data recorded, where comparison is possible, is within the combined error limits. Although the errors associated with the conventional spectrometer are smaller, the synchrotron data is considered more representative as the sample was flowed continuously and unlike in the conventional experiments, was at room temperature for only short periods of time, reducing the likelihood of reaction or breakdown, and also any products of breakdown or reaction would not able to accumulate due to the flowing nature of the system used.

Data has been collected for the first time for spectra below 200nm. Above 200nm, the work can be compared to that of Yao et al (Yao F, 1982) and Harwood et al (Harwood MH, 1998), and the results are compared graphically in figure 4.5 below.
Figure 4.5. Comparison of the photoabsorption spectra obtained by this work (line), that of Yao et al (Yao F, 1982)(solid circles) and that of Harwood et al (Harwood M.H, 1998)(empty circles).

The current work also overlaps, at 240nm, with that of Harwood et Al (Harwood MH, 1993), and the measured cross-section of 0.56 Mb compares favourably with their value of 0.553 Mb. Above 210nm, there is very good agreement with the work of Harwood et al, although at shortest wavelengths there is some divergence seen.

The data presented in this thesis for N$_2$O$_5$ appears to be the best for wavelengths below 240nm, whilst for the range 240-380nm, the data of Harwood et al (Harwood MH, 1993; Harwood MH, 1998) is preferable. Above 380 nm the two studies deviate slightly, and the data of Harwood et al (Harwood MH, 1997) is preferred as they have covered a slightly greater wavelength range. The data sets are shown logarithmically in figure 4.6 below.
4.4.4 Conclusion.

The VUV spectrum of $\text{N}_2\text{O}_5$ has a featureless broad peak centered around 160nm. It does not exhibit any sharp Rydberg features which are usually seen in spectra in this wavelength range. As $\text{N}_2\text{O}_5$ dissociates both thermally and photolytically (below 200nm (Oh D, 1986) the measurement of a good photoabsorption spectrum is difficult. The broad nature of the spectrum shows that absorption of VUV radiation leads to photodissociation.

The photoabsorption measurements taken of $\text{N}_2\text{O}_5$ in the range 200-240nm are in agreement with recently published data of Harwood et al (Harwood MH, 1998), but not with that previously recommended by NASA and suggest systematic errors of up to 30\% in the NASA recommended cross section values (De More WB, 1997). The values obtained in our work may therefore have a significant effect on calculated $\text{N}_2\text{O}_5$ photolysis rates in the atmosphere at an altitude of 30km, as our cross sections are around 40\% greater and this will lead to greater photolysis rates. The photolysis rates as a function of wavelength are discussed in the conclusion at the end of this chapter.
4.5 Photoabsorption Spectra of Cl₂O.

Due to the importance of chlorine oxides in the chemistry of ozone depletion in the Earth's atmosphere, there is a need to further our knowledge into these compounds. In the work reported here, dichlorine oxide, Cl₂O, was synthesised and its photoabsorption cross section measured. The atmospheric concentrations of Cl₂O are not very high, however, it is involved in reactions of HOCl, the acid anhydride, which is an important atmospheric reservoir of chlorine. It is also involved with ClO, which is central to the catalytic loss processes of ozone in the stratosphere. Cl₂O is also used in the laboratory preparation of ClONO₂, one of the most important atmospheric chlorine reservoirs, by a reaction with N₂O₅.

Photoabsorption of Cl₂O was first studied by Goodeve and Wallace (Goodeve C.F, 1930) and Finkelnburg et al (Finkelnburg W, 1931) in the visible and ultraviolet regions. Measurements have been made more recently by Lin (Lin C.L, 1976) between 2 and 6.5 eV (190nm<λ<640nm) and by Molina and Molina (Molina L.T, 1978) between 2.8 and 6.5 eV (200<λ<450nm) and Knauth et al (Knauth, 1979) in the 2.5–6.2 eV range (200nm<λ<500nm). The photoabsorption spectrum of Cl₂O is continuous and consists of three broad bands, in the 620-500, 500-380 and 380-220nm regions. It is thought these bands stem from the excitation of valence electronic states with associated dissociation (Nickolaisen S.L, 1996). Photoabsorption cross sections from the three recent studies are consistent to within 10%. The photoabsorption spectrum was reported recently by Nee (Nee J.B, 1991) in a higher energy range, 6.2 – 8.3 eV (150nm<λ<200nm), the cross sections being normalised to the values of Lin (Lin C.L, 1976). Nee (Nee J.B, 1991) observed an additional dissociative valence state centered about 7.3 eV and also another higher energy bound electronically excited state whose vibrational structure was analysed by means of a u₂ progression, that of the bending vibrational mode. The character (valence/Rydberg) of this state, was, however, not assigned by Nee (Nee J.B, 1991). Assignment of Rydberg states has not been possible due to the high energy limit of the excitation energy domain investigated, which is about 3eV lower than that of the energy of the molecular ionic ground state.

In the present work, the cross section of Cl₂O is reported on an absolute scale for photon energies between 6.5 and 9.7 eV. Electronic excitation spectra measurements at energies higher than those previously used has allowed the observation and assignment of several
new Rydberg states linked with the ionic ground state and its lowest energy excited states.

4.5.1 Laboratory Preparation of Cl₂O.

Cl₂O is a compound that is extremely unstable at room temperature, and even when stored at 195K is liable to explode due to being very shock, heat and light sensitive. The apparatus used to synthesise it was therefore surrounded by a polycarbonate safety shield, to protect operators in the event of an explosion.

The synthesis of Cl₂O is relatively straight forward, in that it only requires the passing of dry chlorine gas over a mixture of HgO. The HgO (Aldrich, 98%) is packed in alternate layers with glass beads into a glass U-tube. This means of packing prevents coagulation of the HgO and inhibition of gas flow. Glass wool is placed at the tops of both sides of the U-tube to prevent HgO spillage or transfer by gas flow. The U-tube was then surrounded by aluminium foil, to exclude light, preventing photochemical decomposition of the product occurring. After attaching the U-tube, the apparatus was evacuated prior to synthesis. Cl₂ was slowly flowed through the U-tube, and the resulting Cl₂O/Cl₂ mixture passed through a trap maintained at 195K by means of an acetone/dry ice slush. During runs of approximately one hour, the Cl₂O collected in the trap and was clearly seen as a cherry red liquid. Basic purification was carried out using a freeze thaw cycle, whereby the trap was cooled to 77K, any dissolved gasses being forced to de-sorb as the liquid crystallised. A schematic diagram of the apparatus used is shown in figure 4.7 below.
4.5.2 Results.

The spectra recorded were scanned in steps of 0.05nm, in sections of 25nm. Sample pressures were below 0.1 Torr, depending on the absorbance within the energy region under study, and checks were made to ensure line saturation effects were not present. The Cl₂O used was about 90% pure, containing about 10% unreacted chlorine. A technique (previously used with a mixture of O₃ and O₂) to subtract the spectral contribution from chlorine was used to obtain a photoabsorption spectrum that could be wholly attributed to Cl₂O. The technique was to record a pure chlorine spectrum, scale it with a Cl₂ reference peak at 9.688 eV (which was isolated from the Cl₂O bands, and then subtracting the scaled chlorine spectrum from the chlorine contaminated Cl₂O one. The error in the present absolute photoabsorption cross sections is estimated at ± 20%.

A photoabsorption spectrum of Cl₂O contaminated with chlorine, recorded in the 6.5 – 9.7 eV range is shown in figure 4.8 below. A spectrum of Cl₂O after chlorine subtraction is shown in figure 4.9 below. Results and discussions presented here are on the subtracted spectrum.
Data is presented on the photoabsorption cross sections in the measured energy range, 6.5 - 9.7 eV. Comparisons of the absolute cross sections are made with earlier data, where available. The photoabsorption spectrum of Cl$_2$O in the VUV region studied, 6.5 - 9.7 eV, consists of a structureless broad band peaking at 7.25 eV and has several
vibrationally resolved electronic bands superimposed on an absorption quasi-continuum, as seen in figure 4.9. Nee (Nee J.B, 1991) had previously observed the broad band centered at 7.25 eV and assigned it to the excitation of a valence electronic state of dissociative character. Nickolaisen et al (Nickolaisen S.L, 1996) suggested a B\textsubscript{1} symmetry for this valence excited state, although in contrast, Kuwata et al (Kuwata K, 1994) suggested assignment to an A\textsubscript{1} symmetry state. Excitation of other dissociative valence states at higher photon energies probably also occurs such that they overlap with the structured Rydberg bands, as seen in figure 4.9 above.

The electronic bands above 7.5 eV that are vibrationally resolved can be attributed to members of several Rydberg states. Quantum defects, calculated using the Rydberg formula (Mulliken R.S, 1942) 1.21, chapter 1, by a collaboration colleague, Motte-Tolett P.M.) has been taken into account when assigning the Rydberg states, as have the relative band intensities and comparison of the band vibrational structures with ones observed using the spectrum from the photoelectron studies (Comford A.B, 1971). Three energy regions shall be discussed separately below.

**The 7.5 – 8 eV region.**

This band, first reported by Nee (Nee J.B, 1991) has a broad electronic band with well resolved vibrational structure, but had not yet been assigned. An enlarged spectrum in this region is shown in figure 4.10 below.
Figure 4.10. Photoabsorption spectrum of Cl$_2$O in the region of the 4s Rydberg state linked to the ionic ground state. The weak unassigned bands are hot bands.

The vibrational envelope is similar to the ionic ground state (Cornford A.B, 1971). This suggests that the potential energy surfaces of both the excited and the ionic electronic states are similar, such that the excited state is of Rydberg character. This band, 7.5 – 8 eV, is therefore assigned to the excitation of the $^1$B$_1$ (b$_1$4s) state, being the first of the nsa$_1$ series, converging to the ground electronic state of the molecular ion $^2$B$_1$. The quantum defect calculated for this $^1$B$_1$ 4s Rydberg state is 1.98 and is shown in table 4.3 below and figure 4.9 above.
<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Quantum Defect</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.703</td>
<td>1.98</td>
<td>b\textsubscript{1}4sa\textsubscript{1}</td>
</tr>
<tr>
<td>8.685</td>
<td>1.58</td>
<td>b\textsubscript{1}4p</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b\textsubscript{1}4p'</td>
</tr>
<tr>
<td>9.233</td>
<td>0.24</td>
<td>b\textsubscript{1}3d'</td>
</tr>
<tr>
<td>9.438</td>
<td>0.068</td>
<td>b\textsubscript{1}3d</td>
</tr>
<tr>
<td>9.026</td>
<td>1.98</td>
<td>b\textsubscript{2}4sa\textsubscript{1}</td>
</tr>
</tbody>
</table>

Table 4.3. Vertical excitation values, quantum defects and assignment of Rydberg states linked to the ionic electronic ground state X\textsuperscript{2}B\textsubscript{1} and to the first ionic electronic excited state A\textsuperscript{2}B\textsubscript{2}.

Vibrational peak energies are shown in table 4.4 where they are compared with the work of Nee (Nee J.B, 1991).

<table>
<thead>
<tr>
<th>This work (eV)</th>
<th>Nee (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.538</td>
<td>-</td>
</tr>
<tr>
<td>7.581</td>
<td>-</td>
</tr>
<tr>
<td>7.618</td>
<td>7.622</td>
</tr>
<tr>
<td>7.662</td>
<td>7.669</td>
</tr>
<tr>
<td>7.703</td>
<td>7.707</td>
</tr>
<tr>
<td>7.742</td>
<td>7.750</td>
</tr>
<tr>
<td>7.783</td>
<td>7.789</td>
</tr>
<tr>
<td>7.822</td>
<td>7.828</td>
</tr>
<tr>
<td>7.867</td>
<td>7.873</td>
</tr>
<tr>
<td>7.906</td>
<td>7.913</td>
</tr>
<tr>
<td>7.946</td>
<td>7.949</td>
</tr>
<tr>
<td>7.988</td>
<td>7.995</td>
</tr>
<tr>
<td>8.030</td>
<td>8.036</td>
</tr>
<tr>
<td>8.067</td>
<td>-</td>
</tr>
<tr>
<td>8.108</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.4. Energy peak values of the vibrational bands observed in the 7.5 – 8.0 eV energy region of our work, compared to values previously obtained by Nee (Nee J.B, 1991).
The data presented is in good agreement with that of Nee (Nee J.B, 1991), and as seen in table 4.4, there is a good agreement between vibrational peak energies between about 7.6 and 8.0 eV.

Nee assigned this vibrational structure to a vibrational progression in the \( \nu_2 \) bending mode. However, probably more than one vibrational mode is excited in the electronic transition, as intensity alternation is seen in the vibrational bands in the 7.6 – 7.7 eV region, as seen in figure 4.10 above. These bands have therefore been interpreted as two progressions involving the \( \nu_1 \) symmetric stretching mode, namely \( \nu_1 \) and \( \nu_1 + \nu_2 \). A summary of the analysis is shown in table 4.5 below and in figure 4.10 above.

<table>
<thead>
<tr>
<th></th>
<th>( \nu_1 )</th>
<th>( \Delta E(\nu_1 \text{ mode}) )</th>
<th>( \nu_1 + \nu_2 )</th>
<th>( \Delta E(\nu_1 \text{ mode}) )</th>
<th>( \Delta E(\nu_2 \text{ mode}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>4s Rydberg state</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>7.618</td>
<td>-</td>
<td>7.662</td>
<td>-</td>
<td>0.044</td>
</tr>
<tr>
<td>1</td>
<td>7.703</td>
<td>0.085</td>
<td>7.742</td>
<td>0.080</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>7.783</td>
<td>0.080</td>
<td>7.882</td>
<td>0.080</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>7.867</td>
<td>0.084</td>
<td>7.906</td>
<td>0.084</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>7.946</td>
<td>0.079</td>
<td>7.988</td>
<td>0.082</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>8.030</td>
<td>0.084</td>
<td>8.067</td>
<td>0.079</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>8.108</td>
<td>0.078</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Hot bands</strong></td>
<td>7.538</td>
<td>0.080</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.581</td>
<td></td>
<td></td>
<td></td>
<td>0.037</td>
</tr>
<tr>
<td><strong>4p Rydberg state</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( N )</td>
<td>8.552</td>
<td>-</td>
<td>8.597</td>
<td>-</td>
<td>0.045</td>
</tr>
<tr>
<td>( n + 1 )</td>
<td>8.628</td>
<td>0.076</td>
<td>8.666</td>
<td>0.069</td>
<td></td>
</tr>
<tr>
<td>( n + 2 )</td>
<td>8.709</td>
<td>0.081</td>
<td>8.745</td>
<td>0.079</td>
<td></td>
</tr>
<tr>
<td>( n + 3 )</td>
<td>8.793</td>
<td>0.084</td>
<td>8.831</td>
<td>0.086</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.5. Analysis of the vibrational structure associated with the 4s, 4p and 4p' Rydberg states linked to the ionic ground state X²B₁ (energy in eV).

<table>
<thead>
<tr>
<th>4p' Rydberg state</th>
<th>n</th>
<th>n+1</th>
<th>n+2</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8.644</td>
<td>-</td>
<td>8.686</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>8.730</td>
<td>0.086</td>
<td>8.766</td>
<td>0.080</td>
</tr>
<tr>
<td></td>
<td>8.817</td>
<td>0.087</td>
<td>0.087</td>
<td>0.087</td>
</tr>
</tbody>
</table>

The (0-0) electronic transition is assigned to the 7.618 eV peak and the two low intensity bands at the lower energy are attributed to hot bands, confirmed by the low band intensity and the energy spacings from the (0-0) band which match the ν₁ and ν₂ ground state frequencies.

**The 8.5 – 9.1 eV energy region.**

This region is shown enlarged in figure 4.11. The vibrational features of low intensity between 8.5 and 8.85 eV have intensities similar to those observed for the lowest energy 4s Rydberg excited state. These structures are therefore assigned to the excitation of the n = 4 members of the np series that converges to the ionic electronic ground state. Electronic transitions from the 3b₁ molecular orbital to the 4pxb₁ and 4pz₁ orbitals lead to the formation of the optically allowed 4p ¹A₁ and ¹B₁ Rydberg excited states. The 3b₁ → 3pyb₂ electronic transition leads to the formation of a 4p excited Rydberg state with A₂ symmetry which is electric-dipole forbidden. The 8.5 – 8.85 eV vibrational features have been experimentally fitted to four vibrational progressions that are related to the excitation of two b₁4p Rydberg states, 4p and 4p’, as predicted by the selection rules. Quantum defects of about 1.58 are estimated by taking the vertical excitation value as a mean energy value between the lowest vibrational peak and the highest energy vibrational peak in the 4p 8.5-8.85 eV region. This is the method used as the adiabatic excitation energies cannot be obtained from the spectrum. The proposed vibrational analysis is shown in table 4.5 above and 4.11.
Figure 4.11. The VUV photoabsorption spectrum of Cl₂O in the region of 4p and 4p' Rydberg states linked to the ionic ground electronic state and of the 4s Rydberg state linked to the ionic first excited electronic state.

The band that is centered around 9eV has a vibrational envelope different to those of the 4sₐ₁ and 4p, 4p' Rydberg states that are associated with the ionic ground state. The analysis of the vibrational structure is shown in table 4.6 below, as a progression involving the excitation of the ν₂ bending mode, with a frequency of about 0.035 eV, compared to an electronic ground state frequency of around 0.037 eV.

<table>
<thead>
<tr>
<th>n</th>
<th>mν₂</th>
<th>ΔE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.860</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>8.895</td>
<td>0.035</td>
</tr>
<tr>
<td>2</td>
<td>8.929</td>
<td>0.034</td>
</tr>
<tr>
<td>3</td>
<td>8.962</td>
<td>0.033</td>
</tr>
<tr>
<td>4</td>
<td>8.995</td>
<td>0.033</td>
</tr>
<tr>
<td>5</td>
<td>9.026</td>
<td>0.031</td>
</tr>
<tr>
<td>6</td>
<td>9.026</td>
<td>0.030</td>
</tr>
<tr>
<td>7</td>
<td>9.086</td>
<td>0.030</td>
</tr>
<tr>
<td>8</td>
<td>(9.110)</td>
<td>(0.024)</td>
</tr>
</tbody>
</table>

Table 4.6. Analysis of the vibrational structure associated with the ^1B₂ (b₂4s) Rydberg excited state (transition 7b₂ → 4sₐ₁). Energies in eV.
The profile of the band is similar to the second band in the photoelectron spectrum (Comford A.B, 1971). Therefore the 8.6-9.1 eV electronic band has been assigned to the excitation of the first member of nsa_1 Rydberg series converging to the first excited electronic state of the molecular ion A^2 B_2 as seen in figure 2. The quantum defect is calculated to be 1.98, shown in table 1.

The 9.1 – 9.7 eV photon energy region.
This region is shown enlarged in figure 4.12.

![Figure 4.12. The VUV photoabsorption spectrum of Cl_2O in the region of the 3d Rydberg state linked to the ionic ground electronic state.](image)

This region consists a few low intensity peaks in the region 9.1 to 9.35 eV and with a high intensity band between 9.35 and 9.7 eV. The high intensity electronic band between 9.35 and 9.7 eV has a vibrational profile similar to that of the three 4sa_1, 4p and 4p' (3b_1^{-1}) Rydberg states and has therefore been assigned to excitation of the n = 3 term of the nd Rydberg series that converges to the X^2B_1 electronic state with a quantum defect of 0.068, seen in table 4.3 and figure 4.9 above. The vibrational analysis involves
the same $\nu_1$ and $\nu_1 + \nu_2$ vibrational progressions as in the lowest 4sa$_1$, 4p and 4p’ Rydberg states which are detailed in table 4.7 below.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\nu_1$</th>
<th>$\Delta E(\nu_1 \text{ mode})$</th>
<th>$\nu_1 + \nu_2$</th>
<th>$\Delta E(\nu_1 \text{ mode})$</th>
<th>$\Delta E(\nu_2 \text{ mode})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9.358</td>
<td>-</td>
<td>9.398</td>
<td>-</td>
<td>0.040</td>
</tr>
<tr>
<td>1</td>
<td>9.438</td>
<td>0.080</td>
<td>9.477</td>
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<tr>
<td>2</td>
<td>9.520</td>
<td>0.082</td>
<td>9.558</td>
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</tr>
<tr>
<td>3</td>
<td>9.594</td>
<td>0.074</td>
<td>9.635</td>
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</tr>
<tr>
<td>4</td>
<td>9.675</td>
<td>0.081</td>
<td>9.715</td>
<td>0.080</td>
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<tr>
<td>hot bands</td>
<td>9.280</td>
<td>0.078</td>
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<td></td>
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<tr>
<td></td>
<td>9.323</td>
<td></td>
<td></td>
<td>0.035</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.7. Analysis of the 9.25 – 9.7 eV vibrational structure associated with the observed 3d Rydberg excited state linked to the ionic ground state X$^2$B$_1$. Energies in eV.

The $n = 5$ member of the nsa$_1$ Rydberg series that converges to X$^2$B$_1$ has been calculated using a value for the quantum defect of 1.98 to lie around 9.52 eV and is probably the cause for the discontinuity in the relative intensity distribution of the vibrational peaks around 9.5 eV. As the intensity of the terms within a Rydberg series is predicted to decrease with $n^3$, this 5sa$_1$ Rydberg excited state may not perturb the 3d vibrational progressions. Excitation of the $n = 4$ term of the nsa$_1$ Rydberg series that converges to the second ionic excited state B$^2$A$_1$ is expected around 9.3 eV and probably underlies the 9.35 – 9.7 eV band. The lowest, 4sa$_1$, Rydberg state associated with the C$^2$A$_2$ ionic state should be around 9.5 eV, but owing to it being symmetry forbidden, it will not be seen in the photoabsorption spectrum. The low intensity peaks in the 9.1 – 9.25 eV region have been assigned to vibrational structures associated with one or more electronic transitions from the outermost molecular orbital 3b$_1$ to other 3d Rydberg orbitals named 3d’, as seen in table 4.7 and figure 4.9 above. The highest peak, at 9.233 eV has given a quantum defect value of 0.24.

Electronic transitions from the 3b$_1$ molecular orbital to 3dx$_{xy}$, 3dx$_{xz}$, 3dz$^2$ and 3dx$^2$-y$^2$ can lead to four 3d Rydberg singlet excited states, $^1$B$_2$, $^1$A$_1$, $^1$B$_1$ and $^1$B$_1$ allowed by the symmetry selection rules, while the 3b$_1$ $\rightarrow$ 3dyz electronic transition is electric dipole selection rule forbidden.
Absolute cross section comparisons.
The absolute cross sections of Cl₂O above 200nm are well known (Lin C.L, 1976; Molina L.T, 1978; Knauth H.D, 1979). However, only one previous measurement has been carried out by Nee (Nee J.B, 1991) of the Cl₂O photoabsorption cross section in the region of 150 – 200nm (6.2 – 8.3 eV).

Correlation between this work and that of Nee (Nee J.B, 1991) is quite good and is within the error bars of the two experiments. (±20%). When comparing the overall shape of our spectra with that of Nee (Nee J.B, 1991), it appears that at shorter wavelengths, in the region of higher vibrational levels of the lowest energy 4s Rydberg state, the data of Nee are affected by some sort of optical transmission limit.

The absolute value for the cross section of some peaks can be affected by the experimental resolution of the apparatus and hence be underestimated. To allow a comparison point with future works independent of the experimental resolution, the oscillator strengths for the various bands in the photoabsorption spectrum are summarised in table 4.8 below.

<table>
<thead>
<tr>
<th>Energy range (E₁ to E₂ in eV)</th>
<th>Oscillator strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.501 – 7.501</td>
<td>0.0759</td>
</tr>
<tr>
<td>7.501 – 8.150</td>
<td>0.0843</td>
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<tr>
<td>8.150 – 9.200</td>
<td>0.188</td>
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<tr>
<td>9.200 – 9.745</td>
<td>0.156</td>
</tr>
</tbody>
</table>

Table 4.8. Oscillator strengths for band structures observed in the 6.5 – 9.7 eV photoabsorption spectrum of Cl₂O.

4.6 Photoabsorption Spectra of ClONO₂.
The experiments on chlorine nitrate ClONO₂ were performed in collaboration with various co-workers, and this resulted in various different techniques being used to study chlorine nitrate. Photoabsorption measurements are discussed in this section, with an overview of electron energy loss, EEL, measurements for comparison. Our co-workers also carried out experiments with a photoelectron spectrometer and a trapped electron spectrometer and anion detector. The results from these techniques differ slightly but
are in agreement with earlier published data, where available, and are summarised in N.J. Mason et al (Mason N.J, 2001).

4.6.1 Laboratory Synthesis of ClONO₂.

ClONO₂ is synthesised by allowing a mixture of N₂O₅ and Cl₂O to warm up from 195K to 273K whilst contained in a sealed trap, over a period of around 12 to 15 hours, according to equation 4.29 below.

\[
\text{Cl}_2\text{O} + \text{N}_2\text{O}_5 \rightarrow 2 \text{ClONO}_2
\]  

(4.29)

The resultant mixture of products is predominantly that of Cl₂ and ClONO₂, a clear liquid with a strongly saturated yellow colour.

The means of introducing both reactants into the same reaction vessel (trap) was as follows. N₂O₅ was prepared in a trap as described above in section 4.4.1. The trap was then attached to a trap-to-trap distillation apparatus, shown in figure 4.13 below, in position B. A trap containing liquid Cl₂O was then attached to position A and both traps cooled with liquid nitrogen. All the valves except V1 and V3 were then opened and the entire system pumped on under vacuum, to remove any volatiles or dissolved gases in the samples. With the vacuum pump running, valve V2 was closed, and the trap in position A was allowed to slowly warm, causing the Cl₂O vapour released to be drawn through the apparatus and into the second trap B, where the liquid nitrogen temperature caused the Cl₂O to sublime.
Purification of the ClONO$_2$ was achieved by trap-to-trap distillation to remove molecular chlorine with a resulting yield of greater than 90% ClONO$_2$ seen as a pale yellow / green liquid. Synthesis of the reactants, N$_2$O$_5$ and Cl$_2$O was as described in sections 4.4.1 and 4.5 above. Purity of ClONO$_2$ samples created was monitored at 240nm using a standard laboratory spectrometer, the Kontron Uvikon 860. The cross section derived using the spectrometer, $1.04 \times 10^{-18}$ cm$^2$, matches the recommended NASA value of $1.04 \times 10^{-18}$ cm$^2$.

4.6.2 Results.

Synchrotron photoabsorption measurements were made between 300 and 137 nm (4.1 - 9.0 eV) in a continuously flowing cell capped with LiF windows. The path length was 16cm, and a step size of 0.5nm was used. Further experiments were made using a Kontron Uvikon 860 UV-Vis spectrometer at the University of Reading and also a Bruker IFS 120HR Fourier Transform spectrometer at the Molecular Spectroscopy Facility at the Rutherford Appleton Laboratory.
Laboratory, down to wavelengths as short as 260nm. Further details are available in N.J. Mason et al (Mason N.J, 2001).

The VUV photoabsorption spectrum measured over the range 4.1 to 9.0 eV is shown in figure 4.14 below.

![Graph of VUV photoabsorption spectrum](image)

Figure 4.14. The VUV photoabsorption spectrum of chlorine nitrate between 240 and 120nm recorded on the DLMSAA. Cross sections obtained for three energies using the constant pressure method are shown as Δs.

The spectrum is featureless below 6.2 eV, exhibiting a continuum which centers around 5.77 eV. Above about 6 eV, the cross section rises steeply. The spectral profile is in agreement with the work of Burkholder et al using a laboratory UV-Vis spectrometer (Burkholder J.B, 1994), which form the basis of NASA recommendations. Data taken using the conventional spectrometer and the fourier transform spectrometer as shown compared (above 210nm) in figure 15 below. The data presented is the first to be measured above 6.2 eV, apart that of Rowland et al (Rowland F.S, 1976) who measured photoabsorption cross sections up to 6.8eV. The spectrum has a second broad band, between 6.2 and 9.0 eV, centered around 8.0 eV, with a small shoulder at around 7.1
eV. There is a minimum at around 8.65 eV, after which the cross section rises at higher energies, which being out of range for the synchrotron measurements, are shown by the EEL data, discussed below. As a precaution against saturation effects in the Daresbury data, the term $\ln(I_o/I_t)$ (from the Beer Lambert Law, equation 2.3, expressed as equation 2.4 for the purposes of calculating cross sections) was obtained as a function of pressure at three fixed wavelengths. The linear pressure plot was then used to calculate the cross sections at the three wavelengths. Cross sections at the wavelengths used for the fixed pressure measurements, shown as triangles in figure 4.14 above agree with the cross sections obtained, confirming that the pressures used were sufficiently low to eliminate the effects of saturation.

A comparison between photoabsorption spectra measured using the Daresbury, Reading and Rutherford Appleton Laboratory instruments is shown figure 4.15 below.

![Photoabsorption cross sections obtained using various optical techniques.](image)

Figure 4.15. Photoabsorption cross sections obtained using various optical techniques. Data collected from the UV-Vis spectrometer and fourier transform spectrometer are shown in table 4.9 below. Data from the synchrotron studies is also shown in table 4.10 below.
<table>
<thead>
<tr>
<th>λ/nm</th>
<th>Energy/eV</th>
<th>VUV cross-section/Mb</th>
</tr>
</thead>
<tbody>
<tr>
<td>210</td>
<td>5.90</td>
<td>3.18</td>
</tr>
<tr>
<td>215</td>
<td>5.76</td>
<td>3.42</td>
</tr>
<tr>
<td>220</td>
<td>5.63</td>
<td>3.28</td>
</tr>
<tr>
<td>225</td>
<td>5.51</td>
<td>2.71</td>
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<tr>
<td>230</td>
<td>5.39</td>
<td>2.04</td>
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<td>235</td>
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<td>5.17</td>
<td>1.03</td>
</tr>
<tr>
<td>245</td>
<td>5.06</td>
<td>0.75</td>
</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>260</td>
<td>4.77</td>
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</tr>
<tr>
<td>265</td>
<td>4.68</td>
<td>0.26</td>
</tr>
<tr>
<td>270</td>
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<tr>
<td>275</td>
<td>4.51</td>
<td>0.16</td>
</tr>
<tr>
<td>280</td>
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<tr>
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<td>0.08</td>
</tr>
<tr>
<td>290</td>
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<tr>
<td>295</td>
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<td>0.04</td>
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<tr>
<td>300</td>
<td>4.13</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 4.9. The Photoabsorption cross sections for chlorine nitrate recorded using a laboratory UV-Vis spectrometer at Reading University (210nm<λ<260nm) and a Fourier Transform spectrometer at Rutherford Appleton Laboratory (265nm<λ<300nm).

<table>
<thead>
<tr>
<th>λ/nm</th>
<th>Energy/eV</th>
<th>VUV cross-section / Mb</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>8.85</td>
<td>18.43</td>
</tr>
<tr>
<td>145</td>
<td>8.55</td>
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<td>23.11</td>
</tr>
<tr>
<td>155</td>
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<tr>
<td>160</td>
<td>7.75</td>
<td>23.93</td>
</tr>
<tr>
<td>165</td>
<td>7.51</td>
<td>20.65</td>
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<td>Temperature</td>
<td>Cross Section 1</td>
<td>Cross Section 2</td>
</tr>
<tr>
<td>-------------</td>
<td>----------------</td>
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<td>2.28</td>
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<td>235</td>
<td>5.27</td>
<td>1.66</td>
</tr>
<tr>
<td>240</td>
<td>5.16</td>
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<td>0.96</td>
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<td>250</td>
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<td>0.81</td>
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<td>4.86</td>
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<td>0.22</td>
</tr>
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<tr>
<td>300</td>
<td>4.13</td>
<td>0.07</td>
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</table>

Table 4.10 Photoabsorption cross sections obtained using the DLMSAA.

Figure 4.15 shows that Daresbury cross sections are higher than those of the other measurements, in the longer wavelength, higher energy regions. The error bars are however high at these cross sections as the absorbances measured were very low. The
Fourier transform and conventional spectrometers gave the best cross sections below 210nm (5.9 eV), and were carried out at relatively high resolution (~0.025nm), although no fine structure was seen.

Figure 4.16 below gives a logarithmic plot comparison of the photoabsorption cross sections discussed above along with NASA recommended values for atmospheric modelling as well as those of Rowland et al (Rowland F.S, 1976) and EEL data.

Figure 4.16. Comparison of cross-section data acquired using a variety of experimental techniques described in the text.

Generally, agreement between the data sets is good, however, there are discrepancies around the 6.1 eV region, where the cross section has a minimum point. In this region, the Daresbury data is about 20% lower than NASA recommended values, whilst the EEL data is about 20% higher. The values of Rowland et al (Rowland F.S, 1976) extend up until 6.52 eV (190nm) where they are around 30% higher than the present values. The general trend, is, however similar with increasing excitation energy.

Electron energy loss spectrometers cross an electron beam (of well defined energy - almost monochromatic) with a target gas jet and collect and energy analyse electrons scattered through small angles centered around 0°. Experiments of this kind involving inelastic electron-molecule scattering can be used to determine photoabsorption cross sections, provided certain criteria are met. At high incident electron energies, the first Born approximation may be used through which the generalised oscillator strength, GOS, was introduced (Inoeuli M, 1971). The DOS is a means of correlating optically measured cross sections with those of electron scattering (Electron Energy Loss, EEL), in the limit of zero momentum transfer (Huebner R.H, 1973). The required conditions are met experimentally when the incident electron kinetic energy, T, is sufficiently high, the electron to target energy transfer, E, is moderate (E/T < ~10%), and the scattering angle is small (θs ~ 0°). The oscillator strength of an absorption band, a dimensionless property, can be determined using the equation:

\[
\text{Oscillator Strength} = f = \int \frac{df}{dE} \, dE
\]  

(4.30)

The differential oscillator spectrum, derived from electron energy loss data using high energy incident electrons, is shown in figure 4.17 as a comparison with photoabsorption DLMSAA data, and the data is shown in table 4.11 below.
Figure 4.17 Comparison of EELs data with that of the photoabsorption measurements taken at the DLMSAA.

<table>
<thead>
<tr>
<th>(\lambda/\text{nm})</th>
<th>Electron energy/eV</th>
<th>Cross section/Mb</th>
</tr>
</thead>
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<tr>
<td>247.8</td>
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</tr>
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</tr>
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</tr>
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</tr>
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<td>5.80</td>
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</tr>
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</tr>
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<td>91.2</td>
<td>13.60</td>
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</tbody>
</table>
An energy of 5.4 eV was used to normalise the DOS spectrum using the results of (Burkholder J.B, 1994). The DOS and photoabsorption data agree within the combined error limits, as shown in figure 4.16 above. At energies above the cut-off of the photoabsorption spectrum, the EEL spectrum exhibits a strong maximum at 9.26 eV, with other features seen at 9.38, 9.74, 10.66, 10.93, 11.47 and 12.98 eV.

<table>
<thead>
<tr>
<th>89.8</th>
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</tr>
</thead>
<tbody>
<tr>
<td>88.6</td>
<td>14.00</td>
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</tr>
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</table>

Table 4.11. Comparison of EEL and DLMSAA data.

4.7 Conclusion.
The photoabsorption cross sections for three molecules relevant to ozone depletion have been measured. The measurements of the photoabsorption cross sections of N\textsubscript{2}O\textsubscript{5} in the 200-240nm region are in agreement with recently published results from Harwood et al (Harwood M.H, 1998), but not with that of others (De More W.B, 1997). Comparisons indicate errors of up to 30% in the NASA recommended values for the cross sections (Yao F, 1982). It is believed that our data have been shown to be more correct than that of the NASA data, and this will have a significant effect on calculated photolysis rates at 30 km. The broad featureless nature of the spectrum in the VUV region implies that dissociation probably accompanies absorption throughout this spectral region.

With regards to Cl\textsubscript{2}O, much effort was made to create a pure sample. No evidence was found to suggest the presence of impurities or decomposition products such as Cl\textsubscript{2}, and the spectra obtained are consistent with literature data. This serves both to create a benchmark for sample purity, and as a check of previous data.

The spectra of ClONO\textsubscript{2} were the first above 6.2 eV, apart from that of Rowland et al (Rowland F.S, 1976), who measured photoabsorption cross sections up to 6.8 eV. Data gathered in the previously unstudied energy region show a peak at 8 eV, although this has no effect on photolysis rates in the stratosphere as the actinic flux below 180nm (6.9 eV) is negligible.

The data measured have been used to calculate photolysis rates according to the equation:
Photolysis rate = $I_a \sigma$

(4.31)

Where $I_a$ is the actinic flux at a given altitude, and $\sigma$ is the cross-section.

The photolysis rates for N$_2$O$_5$, Cl$_2$O and ClONO$_2$ have been calculated and are shown in figures 4.18, 4.19 and 4.20 below.

![Photolysis Rates of N$_2$O$_5$ at 50, 40, 30, 20 and 0 km](image)

Figure 4.18. The photolysis rates of N$_2$O$_5$ as a function of wavelength and altitude.
Photolysis Rates of Cl₂O at 50, 40, 30, 20 and 0 km

Figure 4.19. The photolysis rates of Cl₂O as a function of wavelength and altitude.

Photolysis Rates of ClONO₂ at 50, 40, 30, 20 and 0 km

Figure 4.20. The photolysis rates of ClONO₂ as a function of wavelength and altitude.
These photolysis rates give an indication of the altitudes where the destruction rates of atmospheric molecules are at a maximum. The photolysis data indicates that of the three molecules studied, N$_2$O$_5$ has the highest photolysis rates at short wavelengths. Cl$_2$O and ClONO$_2$, however, have high photolysis rates in more than one energy band. The figures also show that the photolysis of these molecules is important in the Stratosphere between 20 and 40 km, especially that of Cl$_2$O, which could form the chlorine radical which may attack ozone. The dependence on the wavelength (energy) of the actinic flux as well as that of altitude may explain how these molecules can be part of a mechanism that transfers nitrogen and chlorine oxides between atmospheric regions in the form of cycles. The data collected may assist in atmospheric models to understand these cycles further.
CHAPTER FIVE

PHOTOABSORPTION STUDIES OF POLYCYCLIC AROMATIC HYDROCARBONS, PAH'S

5.1 Introduction.

Polycyclic Aromatic Hydrocarbons, PAH's are planar molecules made up of benzene rings that have a resemblance to single layer fragments of graphite. They exist in a wide variety of shapes and sizes and are very common in the environment on Earth. They form during the incomplete combustion of most organic materials and are as such continuously being released into the atmosphere and are present in cigarette smoke, bonfire smoke and even fried or grilled food (Gingell, 2000). The purpose of this study, is, however to obtain spectra of PAH's for the benefits of astrophysics. As PAHs are made up of benzene rings, the photoabsorption spectrum of benzene was measured to see if there were any similarities with the spectra of various PAH's. The PAHs that were studied were Napthalene, 2-Methyl-Napthalene, Anthracene, Fluorene and Pyrene. The structures of those compounds studied and compared to benzene, are shown below in figure 5.1.
Molecular structure of Benzene. Often represented as a hexagon (with double bonds) for simplicity.

Napthalene $C_{10}H_8$

2-Methyl-napthalene $C_{11}H_{10}$

Anthracene $C_{14}H_{10}$

Pyrene $C_{16}H_{10}$

Fluorene $C_{13}H_9$

Figure 5.1. Structures of the PAH's (and benzene) studied in this work.
5.1.1 Relevance of PAH's to Astrophysics.

There are several observed phenomena that suggest strongly absorbing and emitting species are present in the Interstellar Medium (ISM). There are unidentified infra-red emission bands at wavelengths that are consistent over many lines of sight, at wavelengths of 3.3, 6.2, 7.7, 8.6 and 11.3 microns (Hudgins D.M, 1999). Although known to be of molecular origin, the molecular species concerned are currently unknown.

Similarly, there are absorption bands in the visible part of the spectrum, known as Diffuse Interstellar Bands, which are consistent in their shape regardless of the line of sight. Their origin is also thought to be molecular, but the species are also unknown.

The well known UV extinction bump, shown in figure 5.2 below, is a very intense UV absorption feature centered around about 220nm (5.6 eV) and is again consistent along many different lines of sight. The cause of the bump remains unknown. The properties of PAH's are such that it is thought that they may be partially or wholly responsible for the effects outlined above.

![Figure 5.2. The UV extinction bump (Zeilik M, 1973). The peak of the bump is centered around 0.21μm (210nm).](image-url)
PAH's have strong absorption bands in the 4-7eV range, which is close to the UV extinction bump at approximately 220nm (5.6 eV). The interest in astrophysics of these compounds has led to a need to gather a complete data set of photoabsorption cross sections for them. Cross sections of these compounds are however difficult to measure owing to their low vapour pressures at room temperature when larger PAH's are in powder form.

5.1.2 Possible formation of PAH's in space.

There are two suggested mechanisms for the formation of PAH's in the ISM. They may form during the collisions between dust grains (Moseley J.B, 1981) composed mainly of graphite and or silicates. During the collision, graphite planes could fracture, releasing PAH's. PAH's may also form through the reactions of small unsaturated hydrocarbons and radicals that are abundant in the remnants of carbon rich stars (Howe D.A, 1994). It is known that PAH's are very stable once formed, and readily re-emit absorbed radiation in the infra-red, hence possibly explaining the infra-red emission bands observed (Cherchneff I, 1989; Flickinger C.G, 1990; Joblin C. 1995; Joblin C, 1994; Kurtz J, 1992). The photoabsorption spectra of PAHs also appear to correspond well with the energy of the UV extinction bump (Zeilik M, 1973) and also PAH cations have absorption bands that coincide with some of the Diffuse Interstellar Bands seen in the visible part of the spectrum (Hudgins D.M, 1994; Szczepanski J, 1993) PAH's with less than about 20 carbon atoms are thought to be photolysed by UV radiation. Larger ones are thought to be dissociated in shocks and in the hot gas clouds in the ISM, on a time scale of around $10^8$ years, comparable to that of cosmic dust grains. Linear (catacondensed) PAH's, ones that are made up of chains of aromatic rings, are less stable than “pericondensed” ones, those which at any given non-edge carbon atom have three aromatic rings around that atom, such as pyrene. To help understand the link between the presence of PAH's in interstellar space and the UV extinction band, measurement / knowledge of the photoabsorption spectra of PAH's is necessary.

5.2 Results.

Data were collected for Benzene, Naphthalene, 2-Methyl naphthalene, Anthracene, Fluorene and Pyrene. The molecules were chosen as each has an extra benzene ring added consecutively, apart from that of fluorine, which being very similar to anthracene
was studied to see the effects of the addition of a non-aromatic, “incomplete” benzene ring, made up of five carbon atoms as opposed to six.

5.2.1 Experimental Method.

When attempting to record photoabsorption spectra for the PAH’s, difficulties were encountered due to the low vapour pressures and high melting points of these compounds. The temperature controlled cell, section 2.7.3, was used to obtain the cross sections. This cell, did, however suffer from several problems. As PAH's have a very low vapour pressure and are a solid at room temperature, they needed to be heated to achieve a high enough vapour pressure to allow photoabsorption measurements to be taken. As most surfaces in contact with the vapour apart from those of the cell walls were at a lower temperature than that of the vapour, condensation of PAH's posed a problem. Condensation occurred on the cell windows, as these could not be heated by any means other than conduction (a "double glazed" type window would create a problem as the heating fluid between would absorb the synchrotron light). The resulting coating was a solid of unknown thickness, resulting in an unquantifiable absorption of light. Condensation also occurred within the apparatus leading to the cell, with a possible problem arising from condensation within the Baratron pressure measurement transducer, possibly leading to unreliable pressure measurements. The effects of this condensation could not be quantified. As a result of the difficulties encountered with these compounds, the estimated error on the cross sections recorded for these molecules was ±30%.

5.2.2 Photoabsorption Cross Section of Benzene.

Before the spectra of PAH's are presented, the spectral features of benzene will be presented, such that comparisons between PAH spectra and that of benzene can be made.

The six carbon atoms on benzene each have a p-orbital which is out of the plane of the benzene ring. These orbitals combine to form π orbitals above and below the plane of the ring, such that the electron density is the highest above and below the internuclear plane. UV photoabsorption spectra of PAH's resemble that of benzene as the delocalised π-orbitals are dominant, such that these molecules have strong photoabsorption features in the 4-7eV range, and exhibit a strong absorption feature close to the energy where benzene has its strongest absorption, peaking at around 7eV.
A photoabsorption spectrum of benzene is shown in figure 5.3 below:

![Photoabsorption Spectrum of Benzene](image-url)

Figure 5.3 The VUV photoabsorption spectrum of benzene (Gingell PhD, 1998).

The structure observed in benzene arises from one electron transitions from the highest filled pi molecular orbitals (1E_{1g}) to the lowest empty pi molecular orbitals (1E_{2u}), that of $\pi \rightarrow \pi^*$ transitions. The most prominent absorption band, that between 6.5 and 7.5 eV is attributed to the $^1E_{2u}$ excited state (Robin M. B, 1975; Nordheim H, 1940). The vibronic structure superimposed on this band has been attributed to the excitation of Rydberg states (Wilkinson P.G, 1956). The features above 8.0 eV have also been attributed to Rydberg states (Duncan A.B.F, 1971). The band between 6.0 and 6.6 eV is attributed to the $^1B_{1u}$ excited singlet state (Robin M. B, 1975; Nordheim H, 1940) and the structure between 4.5 and 5.5 eV is attributed to the $^1B_{2u}$ excited singlet state (Robin M. B, 1975; Nordheim H, 1940).
5.2.3 Photoabsorption Cross Section of Napthalene.

The photoabsorption spectrum of naphthalene is shown in figure 5.4 below.

![Photoabsorption Spectrum of Naphthalene](image)

Figure 5.4. The VUV photoabsorption spectrum of naphthalene.

The spectrum of naphthalene has a very strong resemblance to that of benzene, the difference being a shift in energy of the main peak, attributed to the $\pi\rightarrow\pi^*$ benzenoid transition, towards that of lower energy. There is also a band between about 7 and 8 eV, which is probably due to Rydberg states. The region between 8 and 10 eV does not show any conclusive Rydberg states, unlike that of benzene. Since this region has a band for all the other small aromatics studied, the lack of clear structure is probably due to experimental factors, this being reinforced by the fact that an electron energy loss spectrum recorded by Huebner et al (Huebner R.H, 1972), figure 5.5 below, shows a band (possibly two) between 9.0 and 10.0 eV.
The profile of the photoabsorption spectrum recorded on the DLMSAA is in good agreement with the electron energy loss spectrum of naphthalene recorded by Huebner et al (Huebner R.H, 1972). The spectral features also lie at energies close to those recorded by Huebner et al (Huebner R.H, 1972) strong feature at 5.89eV is attributed to the $^1B_{2u} \leftarrow ^1A_g$ transition by Huebner et al (Huebner R.H, 1972) and this transition's energy is in close agreement with that recorded on the DLMSAA at an energy of 5.84 eV, with a corresponding cross section of 287.5 Mb. The spectrum is also in agreement with a photoabsorption spectrum recorded by Hammond et al (Hammond V.J, 1950), who also reported a shift to lower energy of the benzenoid peak.
5.2.4 Photoabsorption Cross Section of 2-Methyl Napthalene.

The photoabsorption spectrum of 2-methyl napthalene is shown in figure 5.6 below.

![Photoabsorption spectrum of 2-methyl napthalene](image)

Figure 5.6. The VUV photoabsorption spectrum of 2-methyl napthalene.

The spectrum still shows the characteristic benzenoid peak, at 6.8 eV, shifted to the lower energy range as does napthalene. The band at slightly higher energy between 7 and 8 eV is still seen (although this too is shifted to slightly lower energy). The main difference between this spectrum and that of napthalene is a band between 8 and 11 eV, although there is evidence of this band at slightly higher energy in the spectrum of benzene. This band is probably due to $\sigma \rightarrow \sigma$ transitions, and at first may be thought to arise from transitions associated with the methyl group. However, observation of the spectra for the larger (and also benzene), non-methylated PAH's measured also shows this band, and so its origin is probably not of methyl origin. The spectrum is in agreement with a photoabsorption spectrum recorded by Hammond et al (Hammond V.J, 1950).
5.2.5 Photoabsorption Cross Section of Anthracene.

The photoabsorption spectrum of anthracene is shown in figure 5.7 below.

![Photoabsorption spectrum of anthracene](image)

Figure 5.7 The VUV photoabsorption spectrum of anthracene.

The spectrum of anthracene shows the benzenoid peak which is again shifted towards lower energy. The bands between 7 and 8 eV and 8 and 11 eV remain in the same energy as for 2 methyl naphthalene. Although the overall cross section is lower, there are no appreciable differences between the spectrum of 2methyl naphthalene and that of anthracene. There are however, slightly better resolved structures in the bands between 7 and 11 eV. The shape of the spectrum agrees with that of that previously recorded (Kitagawa T, 1968), although our spectrum is better resolved.
5.2.6 Photoabsorption Cross Section of Fluorene.

The photoabsorption spectrum of fluorene is shown in figure 5.8 below.

![Photoabsorption spectrum of fluorene](image)

Figure 5.8. The photoabsorption spectrum of fluorene.

The spectrum of fluorene is significantly different from the other PAHs studied. The differences between the spectrum of fluorene and that of the other PAH's is probably due to the presence of a non-aromatic (5 membered) carbon atom ring. This may affect the electron distribution such that the delocalised \( \pi \) electrons no longer dominate the spectrum. The benzenoid peak is still observed, at 5.7 eV, and is shifted to lower energy which is consistent with the spectra observed for the other PAH's. The absorption band that is observed between 7 and 8 eV is similar to those seen in naphthalene, 2 methyl naphthalene, anthracene and possibly pyrene. There however substantial differences at the lower energy part of the spectrum. Transitions are seen to occur at around 4.0 and 4.6 eV, and a structured band is seen between 2.8 and 4.0 eV. These features are absent in the spectra of the other PAH's and may therefore be attributed to transitions associated with the incomplete 5 membered benzene ring.
5.2.7 Photoabsorption Cross Section of Pyrene.

The photoabsorption spectrum of pyrene is shown in figure 5.9 below.

![Photoabsorption spectrum of pyrene](image)

Figure 5.9 The VUV photoabsorption spectrum of pyrene.

The photoabsorption spectrum of pyrene shows the benzenoid peak shifted back towards the higher energy range, but at a lower energy than that of benzene. The two distinct bands, between 7 and 11 eV that are seen in the spectrum of anthracene (a compound with one less aromatic ring than pyrene) are very much less distinct. A reason for the discrepancy may be that the PAH's studied until pyrene are all linear, catacondensed, aromatics. Pyrene, however, is a "closed", pericondensed molecule. This molecule also shows signs of a benzene like (possibly Rydberg) feature between 5.5 and 6.0 eV. There is no literature data with which to compare the data.

5.3 Comparisons.

The most prominent absorption band of benzene, that between 6.5 and 7.5 eV is due to the \( \pi \rightarrow \pi^* \) transition. This band is prominent in all the spectra, between 5 and 7 eV, except that for fluorene. This band is shifted slightly to lower energy, relative to that of benzene,
in the spectra of the larger PAH molecules. This can probably be attributed to the electrons in the \( \pi \) orbitals being less tightly bound when in the presence of external, non-aromatic, bonds. The shift to lower energy of prominent features as the number of aromatic rings increases is also observed at longer wavelengths in the infra-red spectral region, thus reinforcing the finding in the VUV region. The lack of the benzenoid feature in fluorene is probably due to the presence of a non-aromatic ring. This is made quite clear when comparing the difference in spectra between naphthalene, consisting of two benzene type rings, and that of anthracene, which has three such rings, which display similar spectral characteristics, and that of fluorene, which although possessing a third ring, has one which is not of benzene type, but of only five carbon atoms. All the spectra, except benzene, share a band at around 7 to 8 eV to varying degrees. The lack of this band in benzene suggests that it arises from bonds between an aromatic ring and another ring or group (it cannot be attributed purely to the methyl group or purely to extra aromatic rings, as they both give rise to the band).

All the spectra show that these molecules absorb in the UV extinction bump region to varying degrees. However, the cross sections of PAH's made up of purely aromatic rings are rather low at the extinction energy. When a non-aromatic ring is introduced, the absorption in the extinction region appears to rise. It is possible then, that the UV extinction bump is of PAH origin, possibly mainly from PAH's which contain one or more non-aromatic rings, although fully aromatic PAH's may also contribute. However, as the energy of the benzenoid peak shifts to lower energy with increasing size of PAH molecules, the bump may be in fact caused by large PAH molecules in the ISM. It has also been suggested that the bump is caused by ionised PAH's in the ISM, as PAH's have a low ionisation potential of \(~\)6 eV. It is now believed that PAH's are responsible for the infra-red emission bands seen at 3.3, 6.2, 7.7 8.7 11.3 \( \mu \)m (Hudgins D.M, 1999), as they absorb in the UV and fluoresce at these bands. The isotropic nature of the bands observed suggests that the PAH's are as abundant in the ISM (Hudgins D.M, 1993) as the most abundant polyatomic interstellar molecules known (Allamandola L.J, 1989). Although thought to be ionised (Sloan G.C, 1999) it is not known whether the PAHs are in anionic or cationic form. When subjected to low energy electrons, those of around 100 eV or less, it is found that benzene has a much higher probability of forming an anion than a cation (Fenzlaff H.P, 1984). Cations of benzene can form when subjected to electrons of
energy as low as 1 eV (Christophorou L.G, 1984). In the ISM PAHs may form cations with an affinity similar to benzene as, similar to benzene, they have delocalised \( \pi \) electrons, where the addition of an extra electron does not affect the stability of the molecule sufficiently to cause dissociation.

### 5.4 Conclusion.

Although the photoabsorption spectra of the fully aromatic PAHs studied do show absorption in the region of the UV extinction bump, it is suggested that more PAHs that contain a non-aromatic ring are studied, as the one studied in this work, fluorene, had the highest cross section at the extinction energy. For future work, I suggest the design of an apparatus that allows the fluorescence, in the infra-red, of PAHs to be studied when subjected to VUV radiation, whilst simultaneously recording a photoabsorption spectrum, for the purposes of comparison with known data and subsequent normalisation. This would allow determination of whether there is a tangible link between the infra red emission bands seen, and the UV extinction bump. It would also be useful to carry out the experiments at temperatures found in the ISM, of a few tens of K, such that possible hot bands were avoided, which would not be present in the spectra observed from light that has been sourced from stellar objects and attenuated by ISM molecules.
CHAPTER SIX

PRELIMINARY RESULTS AND FUTURE WORK OF A REMPI AND LIF BASED SYSTEM AND ELECTRON IMPACT DISSOCIATION APPARATUS

6.1 Introduction.
This chapter gives an overview of the results obtained whilst the REMPI chamber was being developed. Specific details are given on experimental findings that were of relevance to the operation and improvement of the REMPI system. A brief description of some preliminary studies aimed at developing a technique for monitoring the emission of NO from biological cells is also discussed.

6.2 Operation and Tuning of the Laser System.
The dye concentration that is recommended in the Continuum Dye Laser Handbook is substantially too high, and although it does give a reasonable power, it results in damage to laser dye containing optics, the cuvettes and capillary. The recommended concentrations for Rhodamine 590 and Rhodamine 610 are stated as being 69.0 and 30.6 mgdm⁻³ for the oscillator, and 34.0 and 12.4 for the amplifier. In practice, however, concentrations of slightly less than half of this are sufficient, whilst still achieving peak output power. It should be noted that absolute concentrations do not need to be known, as during the beam tuning process the dye concentrations in the two reservoirs are altered by adding dye or methanol to achieve optimum conditions. Thus although in theory an optimal concentration could be measured, in practice amounts are added until a good beam power and profile are achieved.
Optimal starting concentrations are about 30 and 15 mgdm⁻³ for the oscillator, and 17 and 6 mgdm⁻³ for the amplifier. Absolute concentrations required will vary according to the positions of the optics, and will therefore vary slightly every time the dye optics are re-tuned.
When high dye concentrations are used, there is a risk of dye deposits forming on the inner surfaces of the cuvettes/capillary, which can lead to optic damage by burning. The handbook solution is to circulate the dye for 20 minutes before admitting pump beam. Practice has shown that this is not effective, and has lead to damaged (burned) optics. The concentration of dye required for maximum power varies inversely with the pump energy. At a given pump beam energy, there is a dye concentration that gives optimal output power. Weak dye solutions will provide insufficient fluorescence to give complete lasing and amplification. Too high a concentration will limit lasing to a small portion of the cell volume.

Dye laser power will also vary, with a maximum, over the operating wavelength range of the dye or mixture of dyes. The output power of a Rhodamine 590/610 mix is documented as being at 579nm, with a drop of ±10% either side of the maximum within the wavelength range of 567 and 599nm. However, when using the reduced concentrations mentioned above (which gave a slightly lower power output, but far superior beam profile quality – essential for doubling and mixing optics), the width of useable output wavelength range within ±10% of the maximum narrowed by about a third, with a greater narrowing observed on the longer wavelength part of the curve. It was found that after a dye change and retuning of the optics the laser would operate with sufficient power for a period of about one month after which there was insufficient power to provide a reliable UV tracking signal. The dye changing procedure outlined in Chapter three was then performed. The effect of dye degradation as a result of exposure to pump beam is shown in figure 6.1 below.
Figure 6.1 Dye laser beam power as a function of wavelength. Dotted line shows reduction in beam power after use of dye laser for 3 days since a new dye change.

6.3 Results Using the Preliminary Chamber.

The preliminary chamber was successfully used to record a REMPI spectrum of NO. Initially, an attempt was made to acquire a REMPI signal at 226.03 nm, a wavelength known to be strongly active in NO. The REMPI spectrum measured between 225.05 and 225.35 nm is shown in figure 6.2 below. The data was acquired using Easyspec software written by Dr. H. Zhao. The software unfortunately refused to work following an upgrade to Windows 95, an upgrade that would not have been carried out if it was known that it would not support the Easyspec software!
6.4 Results Using the New Chamber.

Although a simple plate based REMPI detection system had been shown to work in the preliminary chamber, the new chamber required the configuration of components that had not been used in the preliminary chamber, namely a grid/plate pair (as opposed to two plates), a channeltron detector and finally an electron gun.

6.4.1 Test of the Simple Grid/Plate Pair for the Detection of REMPI Ions.

The optimal detector voltages were found by tuning the laser to a strong REMPI peak, 226.031nm, and adjusting plate grid voltages. A grid voltage of 10V and a detector plate voltage of around 30V were found to give optimal detection efficiency. An NO spectrum using the repeller grid and attractor plate was recorded at a pressure of 3.5 x 10^{-3} mBar, with a step size of 0.005nm per second, over the range of 226.865 to 224.800nm. This demonstrated that the basic plate/grid pair was operational and could be used to create a REMPI spectrum. The software used to create the spectrum displayed the data as if it were an absorption spectrum. This resulted in an inverted......
spectrum, as seen in figure 6.3 below. Note that the spectrum show signs of saturation, seen as near flat bases of the troughs near the shorter wavelength part of the spectrum.

![Graph showing REMPI spectrum measured using a simple plate/grid pair.](image)

Figure 6.3 REMPI spectrum measured using a simple plate/grid pair.

### 6.4.2 Test of Channeltron Based Detector.

Although use of the plates was shown to be sufficient for the detection of NO REMPI at relatively high target gas pressures, operation at lower pressures would lead to a small signal-to-noise ratio using the plate method. For this reason, a channeltron based system needed to be devised. As channeltrons can suffer permanent damage when operated at pressures above $10^{-5}$ mBar, a test needed to be carried out that showed how the REMPI ion signal varies with pressure. During the initial set up period, reverse channeltron voltages were tried in order to measure electrons released from the electron gun, as a test of the operation of the channeltron. These tests showed that the Penning gauge emitted significant quantities of electrons, that the channeltron detected. The gauge was mounted in a line of sight to the channeltron, on the opposite side of the chamber, to minimise gas flow restrictions which could result in pressure measurement time lags and incorrect readings. This "noise" was not a problem as positive ions were to be detected, as in positive ion detection mode, the mouth voltage would repel electrons. Indeed, when detecting NO REMPI ions, the gauge had no effect on the signal seen.
The gauge noise was not a problem in positive ion detection mode, and so no action was taken to remove the source of the noise. Pressure dependency of the NO REMPI signal was measured at a peak REMPI wavelength of 226.031 nm, with a starting pressure of $6.6 \times 10^{-5}$ mBar. The starting pressure was chosen to be slightly lower than the maximum permissible with a channeltron, to allow for any possible pressure measurement errors (exposure of a channeltron, whilst powered up, to excessive pressure can cause immediate, irreversible damage).

The pressure dependency of the NO REMPI signal dropped off as expected, with an exponential drop off towards the lower pressure limit. The erratic nature of the signal seen is due to the low number of counts and the slightly random operation of the channeltron. Although apparently exponential, the curve is in fact a linear decay approaching a noise background at the lower pressure. The pressure/signal plot is shown in figure 6.4 below.

![Figure 6.4 Pressure dependency of the NO REMPI signal.](image)
The operating pressure to be used for future scans was chosen to be in the region of $5 \times 10^{-5}$ mBar, as that was close to the maximum pressure permissible for maximum signal.

Having established a working pressure, in practice the highest that was permissible, the channeltron based detector was tested by acquiring an NO REMPI spectrum. A short high resolution scan was taken between 226.0000 and 226.0620 nm in 0.0005 nm steps. A satisfactory spectrum was achieved, and this is shown in figure 6.5 below.

![Figure 6.5 NO REMPI spectrum acquired using channeltron detector (low count rate).](image)

The count rate, however, was not particularly good. This was improved by bringing the channeltron closer to the grid, and hence to the interaction region, such that the new spacing between the channeltron mouth and grid was 5 mm. This resulted in an increased count rate as shown in figure 6.6 below.
The overall conclusion of this work at present is that to acquire a REMPI spectrum, use of higher pressures and simple ion plates is preferred, as this method gives rise to a spectrum of greater intensity resolution. This is probably due to the fact that at present the channeltron system is not optimised, and the low count rates result in poor signal to noise ratio.

6.5 Electron Impact Dissociation System.

As a result of serious laser damage towards the end of the work, which required the complete replacement of the laser system, caused by a flood in the premises above the laser laboratory, the experimental work for this thesis ended. The electron impact dissociation system was therefore not tested using the laser, but the electron optic components were tested and commissioned. With the electron gun, Faraday cup and REMPI plates installed, the ultimate pressure reached was \(4.0 \times 10^{-7}\) mBar. Switching on the filament, at 2A causes ambient pressure to rise to \(1.1 \times 10^{-5}\) mBar as a result of outgassing. The pressure drops quickly to about \(3 \times 10^{-6}\) mBar when the filament is switched off. Running the filament continuously for several hours allows the materials to fully outgas, and the ultimate pressure reached is actually lower, as compounds that previously outgassed slowly, have been burnt off, allowing an ultimate pressure of \(1.7 \times \)
$10^{-7}$ mBar to be reached. For this reason, during future electron impact dissociation work, gas will only be admitted to the chamber after the filament has been switched on.

Tests were carried out to determine the currents detected on the Faraday cup, as a function of filament current and bias (electron energy). The variation of Faraday cup current as a function of filament current is shown for two energies, 81 eV and 10 eV, in figures 6.7 and 6.8 respectively.

![Figure 6.7. Variation of Faraday cup current as a function of electron gun filament current, at an electron energy of 81 eV.](image)

Figure 6.7. Variation of Faraday cup current as a function of electron gun filament current, at an electron energy of 81 eV.
6.5.1 Electron Impact Dissociation - Suggested Future Studies.

A suggestion for future work is that the apparatus be used to create NO\(^+\) fragments, by means of electron impact dissociation of a suitable molecule, such as CH\(_3\)NO\(_2\). The REMPI system, which is known to be functional, could then be used to detect the fragments. A further development could be the addition of a mass spectrometer to analyse the mass of dissociated molecular fragments.
6.6 Detection of NO Released from Living Muscle Cells by Means of LIF.

The aim of the work carried out was to develop a non-invasive means of measuring NO released from living tissue. The study of NO in humans is of interest as it plays an important role in the body’s fight against infection and the concentration of NO in the blood is a very good indication of a patient’s health.

In the event of a small injury, NO is released locally in concentrations large enough to kill foreign pathogens but not to kill the body’s own cells. When a person becomes seriously injured or intoxificated, the body responds by releasing large quantities of NO, known as going into shock. The purpose of going into shock is to protect the body from either the infection that brought on the shock, or as a precaution against infection that may occur from large open wounds. However, the concentrations of NO released during shock are high enough to cause toxicity in the patient, and can in some cases be fatal (the shock rather than the injury being the cause of death).

The aim of the tests carried out was to initiate investigations that could lead to the development of a non-invasive technique for the measurement of NO concentrations in the blood. The means of detection would be LIF and would require an instrument of fixed wavelength. By using a non-invasive technique, it would be possible to carry out measurements in real time, whereby the instrument would be taken to the patient. Future developments would allow the instrument to be portable, and be easily taken to accident sites for an instant diagnosis.

The investigations were carried out as a side line during the construction of the preliminary LIF/REMPI chamber. Although initially the aim was to measure the release of NO from living muscle cells during a stimulus, this was never achieved as the time budget was exceeded, and work needed to concentrate on the initial research programme.

6.6.1 Preliminary Investigations.

The overall aim was to create a system that could measure the NO that is released by living cells during a stimulus. The measurement technique that was to be employed was
LIF, using UV radiation at 226.03 nm, a wavelength that is known to induce strong LIF transitions in NO. However, before a system could be devised, it was necessary to carry out two basic tests to determine whether such measurements were possible. The first was to quantify the UV laser intensity damage threshold for living cells, and the second was to assess the possibilities of measuring the presence of NO in the form of small bubbles in life sustaining Kreb’s solution.

For damage threshold purposes, two sets of cells were prepared in sample cells, contained in Kreb’s solution, one set being exposed to laser light, and the other set not exposed. The laser damage threshold was found by exposing one set of cells to differing numbers of laser pulses of differing intensity. The cells were then left for 24hrs and were then stained using a dye. Cells which had either been damaged or killed became stained by the dye as their cell walls had become permeable to the dye. By viewing the sets of cells under a microscope, and allowing for a small fraction that would die naturally, it was possible to determine the damage threshold. Premature death caused by incorrect preparation or storage temperature was accounted for, by the set not exposed to the laser. The threshold was found to be surprisingly high, the cells being able to withstand hundreds of 9ns 4mJ pulses. Damage was however seen when cells were exposed to thousands of pulses. This is not a problem as the final system will only need to use small numbers of pulses, at a reduced intensity.

Whilst the threshold work was being carried out, a system to detect NO bubbles in Kreb’s solution was being devised. This involved the building of a light tight enclosure that would contain an x-y translation stage on which was to be mounted the solution under test. The stage consisted of a mount to hold a 10mm square UV transmissive cell, designed to be filled with Kreb’s solution and have NO bubbled through by means of a side mounted narrow bore tube fitted with a fritted glass ending positioned at the base of the cell. NO was to be passed through the tube, to be released as small bubbles, which would rise and be detected. The effect of NO dissolving and going into solution was also to be observed using LIF techniques.

An LIF spectrum was measured to determine whether an LIF process was taking place. NO was admitted into the chamber, and the laser run at a fixed wavelength, 225 nm, known to cause LIF excitations in NO, whilst scanning the monochromator manually.
This resulted in a photomultiplier signal versus monochromator wavelength plot, which clearly shows both the pump laser signal and the LIF signal. The difference in intensities of the two is low, as despite the pump laser power being very high, the pump laser light detected is that scattered through 90° from a very low number density of gas and dust particles. A plot of pump laser and fluorescence signal is shown in figure 6.9 below.

![Figure 6.9. LIF and pump laser signal measured during test of LIF system.](image)

**6.6.2 Detection of Biological NO – Future Work.**

Having established that UV laser light can be used to irradiate cells without causing immediate damage, future work could concentrate on investigations of detecting NO in the form of bubbles and in solution. The apparatus required was built during the work carried out for this thesis, and only required the addition of a tube with sintered glass end and NO source for use with the Kreb's solution cell. Before any LIF measurements can be taken, the degree to which Kreb's solution absorbs UV laser light needs to be measured. At the time of apparatus construction, a quick, non quantitive test showed that a 10mm path length did attenuate the laser beam by about half. Having measured the attenuation, LIF studies should be carried out using freshly prepared solution, with NO bubbled through it, noting any changes in absorption/LIF that may occur as the amount of NO dissolved in solution increases. Another test should concentrate on how absorption and LIF are affected by a solution that is saturated with NO.
The reasons for these simple tests are so that it can be determined whether a practical system could be devised to measure NO as bubbles in a liquid (not feasible if the liquid is so attenuating that neither pump laser can excite, nor LIF can escape), and if attenuation is not a problem, how dissolved NO affects fluorescence (will, for example, a high concentration cause line saturation effects, and if so, how would these be corrected for as the concentration increases with time).

It should be noted, that even if a system is created that can detect NO in bubbles, and corrects for a rise in dissolved NO concentration, this is an ideal situation, far removed from that which would be presented if a patient required real-time non-invasive measurements to be taken. The work described was developed to allow the study of stimulated muscle cells, that release NO during a stimulus. Should the preliminary studies be promising, the entire conceptual design will have to be modified to allow measurement through the skin. Since skin is non uniform, and varies from patient to patient, a system would need to be devised that can measure NO released at the surface of the skin, and to apply a correction (derived using non-invasive skin surface measurements and blood sample measurements) that correlates surface measurements to blood NO concentration.

6.7 Conclusions.

An experimental system was developed and commissioned to study REMPI of molecular targets. However due to a catastrophic flooding of the laboratory only limited results could be obtained and a system built to use REMPI to detect molecular fragments produced by electron induced dissociation could not be completed. A second LIF system was likewise developed and preliminary tests performed using LIF to detect NO emission from live cells. It is expected that with the installation of a new laser system both of these projects will now proceed based upon the pioneering work described in this thesis.
Conclusion

During the work carried out for this thesis, spectroscopic studies were carried out using both synchrotron and laser radiation. The synchrotron work involved measuring the photoabsorption cross sections of N$_2$O$_5$, Cl$_2$O and ClONO$_2$, molecules of importance to atmospheric chemistry. The results have been published in the following papers:

1. Vacuum ultraviolet spectrum of dinitrogen pentoxide.

2. Absolute cross sections for the VUV optical absorption of Cl$_2$O in the 6.5 - 9.7 eV energy range.

3. VUV optical absorption and energy loss spectroscopy of chlorine nitrate.

The synchrotron also used to probe the VUV spectroscopy of PAH molecules, (napthalene, 2-methyl napthalene, anthracene, fluorene, pyrene), believed to have a great significance in astrophysical processes in the Inter Stellar Medium.

A new experimental system has also been developed at UCL for measurement of high resolution LIF and REMPI spectra of simple molecules. Initial results are shown as the system was built and tested. It has been designed to allow expansion into a system capable of measuring electron impact dissociation of molecules by means of REMPI detection of the neutral products.
References

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Appendix 1:
List of Publications.

Published Papers.

**VUV optical absorption and energy loss spectroscopy of chlorine nitrate.**

**Vacuum ultraviolet spectrum of dinitrogen pentoxide.**

**Experimental studies on electron scattering from atoms and molecules: the state of the art.**

**Absolute cross sections for the VUV optical absorption of Cl₂O in the 6.5 - 9.7 eV energy range.**

Papers in preparation.

**High resolution electronic spectroscopy of haloalkanes.**
**Articles.**

**Vacuum ultraviolet spectrum of dinitrogen pentoxide.**

**VUV Absorption spectroscopy of free radicles: OCl.**

**VUV absorption spectroscopy of candidate interstellar molecules.**

**Posters presented at conferences.**

**The study of electron impact induced molecular dissociation by means of resonance enhanced multi-photon ionisation.**

**VUV photoabsorption spectroscopy of polycyclic aromatoc hydrocarbons (PAH's)**

**VUV spectroscopy of simple polycyclic aromatic hydrocarbons.**

**Rydberg state spectroscopy of haloalkanes.**