Laser-induced fluorescence measurements on electron-impact excited molecules.

Murray Ronald. Darrach

University of Windsor

Follow this and additional works at: https://scholar.uwindsor.ca/etd

Recommended Citation
https://scholar.uwindsor.ca/etd/2575

This online database contains the full-text of PhD dissertations and Masters' theses of University of Windsor students from 1954 forward. These documents are made available for personal study and research purposes only, in accordance with the Canadian Copyright Act and the Creative Commons license—CC BY-NC-ND (Attribution, Non-Commercial, No Derivative Works). Under this license, works must always be attributed to the copyright holder (original author), cannot be used for any commercial purposes, and may not be altered. Any other use would require the permission of the copyright holder. Students may inquire about withdrawing their dissertation and/or thesis from this database. For additional inquiries, please contact the repository administrator via email (scholarship@uwindsor.ca) or by telephone at 519-253-3000 ext. 3208.
NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments.

AVIS

La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilming. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopy de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.
LASER INDUCED FLUORESCENCE MEASUREMENTS ON ELECTRON-IMPACT EXCITED MOLECULES

by

Murray Ronald Darrach

A Dissertation submitted to the Faculty of Graduate Studies through the Department of Physics in Partial Fulfillment of the requirements for the Degree of Doctor of Philosophy at The University of Windsor

Windsor, Ontario, Canada 1990
The author has granted an irrevocable non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of his/her thesis by any means and in any form or format, making this thesis available to interested persons.

The author retains ownership of the copyright in his/her thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without his/her permission.

L'auteur a accordé une licence irrévocable et non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de sa thèse de quelque manière et sous quelque forme que ce soit pour mettre des exemplaires de cette thèse à la disposition des personnes intéressées.

L'auteur conserve la propriété du droit d'auteur qui protège sa thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

ISBN 0-315-65157-1
ABSTRACT

An electron-impact excited jet-cooled molecular beam was probed by a tunable dye laser system allowing elucidation of the electron-impact ionization and dissociation processes. This technique has been applied to the study of the rotational ground state and excited state populations of electron-impact excited Na⁺. Following electron-impact dissociation of acetonitrile, water and methanol similar measurements have been performed on the rotational populations of CN(X) and OH(X). We also present results for the absolute cross section for the electron-impact formation of CN(X) from CH₃CN. Measurements have also been performed on the relative cross section for the electron impact dissociation of OH(X) from H₂O and CH₃OH. We have demonstrated the feasibility of the technique and discuss several possible future avenues of research.
This work is lovingly dedicated to my wife Anne Marie whose love and support made all this possible.
ACKNOWLEDGEMENTS

I would like to extend my utmost appreciation and thanks to my supervisor Dr. J.W. McConkey. He has given this author much patient support and guidance in the time during this research. Also his concern for those aspects of life outside of physics has made the last few years much more enjoyable and bearable for the life of all of the graduate students in his employ.

To the machine shop under Mr. W. Grewe and the electronics shop staff under Mr. B. Masse I would like to give my thanks. Without their expert knowledge and technical assistance this experiment would not have been possible. Acknowledgement is also due Dr. P.W. Zetner and Dr. P. Hammond who provided helpful discussions and technical advice.

My thanks to my parents Ronald and Marie Darrach for their love and support and who gave me a home where I could pursue my chosen profession. I must also thank my wife Anne Marie for her assistance in the typing and preparation of this manuscript.

This work was supported by the Natural Sciences and Engineering Research Council of Canada.
TABLE OF CONTENTS

ABSTRACT............................................................................................................................iii
DEDICATION............................................................................................................................iv
ACKNOWLEDGEMENTS..........................................................................................................v

SECTION 1 .............................................................................................................................. 1
  1.1 Introduction .................................................................................................................... 1
  1.2 References ..................................................................................................................... 3

SECTION 2 DESCRIPTION OF THE APPARATUS .............................................................. 5
  2.1 Introduction ................................................................................................................... 5
  2.2 The Laser and Optical Systems ................................................................................... 7
     2.2.1 The Laser System for N₂⁺ and CN Studies ......................................................... 7
     2.2.2 The Laser System for OH Studies ................................................................... 9
     2.2.3 The Data Collection Optics .......................................................................... 13
  2.3 Metastable Detection System ..................................................................................... 18
  2.4 Aspects of the Supersonic Jet Source: ..................................................................... 20
     2.4.1 The Pulsed Valve for N₂⁺ Studies .................................................................. 20
     2.4.2 The Theory of Supersonic Expansion of Gases ............................................ 24
     2.4.3 The Pulsed Valve for CN and OH Studies ..................................................... 32
  2.5 Design and Characteristics of the Electron Optics ................................................... 42
     2.5.1 Design Criteria of the Electron Optics .......................................................... 42
     2.5.2 The Electron Optics ..................................................................................... 47
  2.6 Electronics .................................................................................................................. 53
     2.6.1 Triple Beam Timing Electronics for N₂⁺ Studies ........................................... 53
     2.6.2 Data Collection Electronics for N₂⁺ Spectra .................................................. 56
     2.6.3 Data Collection Electronics for N₂⁺ LIF-TOF Studies .................................... 59
     2.6.4 Data Collection Electronics for CN and OH Studies .................................... 60
  2.7 References .................................................................................................................. 62

SECTION 3 ROTATIONALLY RESOLVED ELECTRON IMPACT IONIZATION OF N₂ IN A SUPersonic JET .......................................................................................................................... 64
  3.1 Introduction ................................................................................................................ 64
  3.2 Theory ......................................................................................................................... 68
  3.3 Results and Discussion .............................................................................................. 73
  3.4 Conclusions ............................................................................................................... 96
  3.5 References ................................................................................................................ 97

SECTION 4 ROTATIONALLY RESOLVED LASER INDUCED FLUORESCENCE STUDIES ON CN X (ν'' = 0, 1) PRODUCED BY ELECTRON IMPACT DISSOCIATION OF ACETONITRILE .......................................................................................................................... 100
  4.1 Introduction ................................................................................................................ 100
  4.2 Results and Discussion .............................................................................................. 103
     4.2.1 Experimental Details .................................................................................... 103
     4.2.2 Laser induced rotational spectra .................................................................. 104
     4.2.3 Absolute Cross Sections ............................................................................. 117

vi
SECTION 1

1.1 INTRODUCTION

The area of electron-impact on atoms and molecules has been a very active field since before the advent of quantum mechanics. Electron-impact phenomena such as that in the classic Franck-Hertz experiment [1] gave concrete proof of the quantized nature of the atom. This area has expanded over the last 50 years to touch almost every field of physics and the advent of lasers has augmented this important tool [2]. Lasers with their narrow bandwidth and high energy selectivity allow the experimenter to probe fine and hyperfine structure within the atom and molecule.

In atomic collision physics the laser can probe the initial and final states of the collision process or prepare the target or projectile in some state. This technique is a sensitive tool to test current theories and has been been used in the area of ion-molecule collisions by Morrison et al.[3] and Mariero et al.[4] who have probed the products of the $H + D_2$ reaction. A highly significant new area is that of providing an excited state target for collision by an electron. the super-elastic, excited state elastic and inelastic cross sections becoming available for measurement. Stebbings et al.[5] discussed the preparation of Rydberg projectiles for the study of atom-atom collisions. Super-elastic scattering has been studied for example by J.J. McClelland et al.[6] in Sodium and by D.F.Trajmar and P.W.Zetner [7] in Barium. This technique is still very new and much interesting physics is yet to be discovered.
In this experiment we explore the perspective of the final product states being probed after electron-molecule collisions. There has been very little work done in this area, most of the final state probing has been done in the area of photo-ionization and photo-dissociation [8-11]. The emission by molecules and their fragments after excitation and/or dissociation by electron-impact has been however an ongoing area of study [12-15]. The dissociation of polyatomic molecules plays an important role in our understanding of chemical bonding and of the interactions between small molecules and radicals. Unlike scattering experiments in which molecular beams are crossed and product yields are determined as functions of laboratory angles, dissociations give us important insight into molecular potential energy surfaces from well-specified initial geometries. In photo-dissociation the dynamics of a fragmentation can be studied because the input energy is accurately known along with a quantization axis for the process defined by the laser polarization. Dissociation by electron-impact at higher energies can proceed via optically allowed transitions, while at near-threshold energies optically forbidden transitions may dominate [14]. In any type of experiment however, measuring the internal state distributions of the products is an informative way of probing the dynamics of the process.

In Section 2 the apparatus is discussed in detail and gives a brief discussion of the evolution of the high-temperature pulse supersonic valve used in this experiment. In Section 3 an investigation into the electron-impact ionization of nitrogen is presented. There has been much discussion on the re-ordering of internal
state distributions after electron-impact ionization and this work we believe has clearly established the relevant features. In Sections 4 and 5 we present the results of an investigation into the electron-impact dissociation of various molecules. Using the laser to probe the ground state rovibronic levels allows us to illuminate the dissociation process. The laser also allows us to probe ground state populations of the fragment radicals and by referencing the fluorescence intensity measurements to known cross-sections, we can quote absolute cross sections for the formation of these radicals. Dissociation cross-sections over the electron-impact energy range of 30-300 eV are given. The last section gives an overview of the results and suggests future directions for the experiment.

1.2 REFERENCES


SECTION 2

DESCRIPTION OF THE APPARATUS

2.1 Introduction

The apparatus consisted of three intersecting beams which defined an interaction region viewed by an arrangement of lenses and a photomultiplier tube, as shown in Fig. 2.1. An electron beam produced by an in-house built electron gun, intersected at approximately 30° with respect to a laser beam produced either by a commercial N₂ or YAG laser-dye laser combination. A freely-expanding gas jet produced by a molecular beam valve then intersected the electron and laser beams at 90° with respect to the plane formed by the electron and laser beams. The electron source and molecular beams valve were mounted on an aluminum block and together with some detection optics were housed in a stainless steel vacuum chamber. The chamber was evacuated by two 6" Edwards Diffstak® oil diffusion pumps. The chamber also contained a LN₂ cold trap, filled under the control of a timed solenoid valve connected to a 50 L LN₂ reservoir. The best vacuum obtained in the chamber was 4 x 10⁻⁷ Torr (untrapped) and 2 x 10⁻⁷ Torr (trapped). An arrangement of three pairs of Helmholtz coils around the chamber, positioned along three mutually orthogonal axes, provided cancellation of the earth's magnetic field inside the interaction region.
Figure 2.1 Block schematic of the experimental apparatus used in the dissociation experiments. Some details of the apparatus such as the vacuum system and detection optics have been omitted for clarity.
2.2 The Laser and Optical Systems

2.2.1 The Laser System for N₂⁺ and CN Studies

A Molectron UV-24 Dl-II nitrogen-pumped dye laser system was used in the N₂⁺ and CN molecular LIF experiments. The nitrogen laser yielded about 8mJ/pulse at a repetition rate of 25 pulses per second. The 3371 Å radiation from the nitrogen laser pumped the dye laser, which consisted of an oscillator of Hansch design [1] with an additional amplifier stage also transversely pumped. Quartz cuvettes held the dye solution in which magnetically coupled stirrers agitated the dye to dissipate the heat produced by the UV pumping pulse. The dyes used, and the concentrations thereof, were those recommended by the Exciton Chemical Co. Ltd. (according to the tuning curves supplied by Molectron Corp.). Wavelength selection was accomplished by means of a rotatable reflective diffraction grating, which serves as an end reflector in the resonant oscillator cavity. The grating was coupled through a sine drive to a system of gears and belts to either a stepper motor (for automated scanning) or a hand crank (for manual adjustment).

When using the dye laser to produce laser light in the near ultraviolet, it was not possible to measure the mode structure of the laser pulse. However, we can make some crude predictions [2-4]. The axial mode spacing, to a first approximation, is given by the free spectral range (FSR) of the (passive) laser resonant cavity

\[ \Delta \nu = \frac{c}{2d} \quad (2.1) \]
where $d$ is the length of the resonator cavity. For our cavity, the resonator length is 25 cm, yielding $\Delta \nu = 0.6 \; GHz$. The frequency spectrum of the laser actually consists of a random superposition of many modes, which fluctuate in time. This time dependance arises from frequency jitter due to acoustical coupling to the resonator, changes in the refractive index of the dye solution due to heating, etc...

The linewidth of each mode is given by

$$\delta \nu = \Delta \nu \frac{1-G(\nu)}{2 \pi \sqrt{G(\nu)}}$$

(2.2)

where $G(\nu)$ is the frequency dependent gain of the laser dye solution. The gain is defined by

$$G(\nu) = \exp(-\alpha(\nu) L - \gamma(\nu))$$

(2.3)

where $\alpha(\nu)$ is the absorption coefficient of the dye solution, $L$ is the length of the dye solution, and $\exp(-\gamma(\nu))$ is the total losses per round trip through the resonator.

For the condition of laser oscillation, $G(\nu) = 1$ which implies $\delta \nu = 0$.

We therefore assume the resonator mode linewidth to be given by the Fourier transform limit of a 7 ns pulse, and we get $\delta \nu \approx 0.2 GHz$. If all modes can co-exist within the laser linewidth of about 15 GHz, then we have about 25 simultaneously oscillating modes per laser pulse. When the dye laser was used to produce 6000 Å laser radiation, the mode structure was measured using a Fabry-
Perot airspaced etalon with a free spectral range of 1 cm⁻¹. It was observed that approximately 10 - 15 modes were simultaneously operating under the gain envelope of the diffraction grating.

2.2.2 The Laser System for OH Studies

During the investigations on OH radicals it was necessary to use a more powerful laser to make sufficiently intense ultraviolet radiation to pump the OH \( A \quad ^2\Sigma^+(\nu' = 0) - X^2\Pi(\nu'' = 0) \) transition at 3080 Å. The laser system consisted of a Continuum model YG-661-30 YAG laser capable of delivering 600 mJ/pulse at 1064 nm and a Continuum model TDL60 flowing dye laser. After frequency doubling the YAG pumped-dye laser combination yielded up to 40 mJ/pulse at 3080 Å. This was a substantial improvement over the Na pumped-dye laser which delivered at most 0.25 mJ/pulse at the same wavelength. Further specifications of the YAG and dye lasers are given in Table 2.1. Wavelength tuning was accomplished by communicating to the TDL60 dye laser over an RS-232 serial port in an IBM XT computer. The dye laser was a three stage design; a Moya-geometry oscillator, a preamplifier and a final amplification stage. The oscillator consisted of a quad-prism beam expander, a grating fixed for grazing incidence, a rotatable mirror and a totally reflective mirror as the output coupler. Amplified spontaneous emission (ASE) is reduced by the output coupler being placed off-axis of the main direction of emission. The standard configuration consisted of one 2400 lines/mm grating, with a second grating being mountable for reduced linewidth if necessary. Frequency doubling of the dye laser radiation was achieved by the use of a KDP
angle-tuned crystal.

<table>
<thead>
<tr>
<th>Continuum YG-661-30 YAG laser</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Energy (mJ/pulse)</strong></td>
</tr>
<tr>
<td>1064 nm</td>
</tr>
<tr>
<td>532 nm</td>
</tr>
<tr>
<td>355 nm</td>
</tr>
<tr>
<td><strong>Pulsewidth (ns)</strong></td>
</tr>
<tr>
<td>1064 nm</td>
</tr>
<tr>
<td>532 nm</td>
</tr>
<tr>
<td>355 nm</td>
</tr>
<tr>
<td><strong>Energy Stability</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Continuum YG-661-30 YAG laser + TDL-60 dye laser</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Peak of R640 @ 620 nm</strong></td>
</tr>
<tr>
<td>Frequency doubled @ 310 nm</td>
</tr>
<tr>
<td>Single grating linewidth</td>
</tr>
<tr>
<td>Dual grating linewidth</td>
</tr>
<tr>
<td>ASE at 620 nm</td>
</tr>
</tbody>
</table>
Table 2.1 Characteristics of the YAG pumped-dye laser system.

Either dye laser beam was passed through a series of optical components to ensure high beam quality in the interaction region, minimize hot spots and ensure amplitude stability. The laser beam emerging from the dye laser was passed through a variable iris diaphragm, a beam reducer, a pinhole (200 – 600 μm), a collimating lens, a second variable iris diaphragm, two steering prisms, a third variable iris diaphragm and finally a second beam reducer. Both entrance and exit windows on the vacuum chamber were Brewster angled Quartz windows, to minimize laser scatter. In most cases there were also two further 1.5 mm collimating pinholes (sooted to minimize scatter) mounted on the interaction block to provide precise positioning of the laser. In experiments where the polarization of the laser radiation was to be varied, an arrangement of components consisting of a $\frac{\lambda}{2}$ plate and a polarizing Glan-air prism, was inserted between the third variable iris diaphragm and the second beam reducer. All lens components were made of fused silica, to maximize transmitted laser power. The details of the laser optical system are shown in fig.2.2.

The first beam reducer consisted of two confocal positive lenses of 20 cm and 10 cm focal lengths placed in a telescope arrangement. This increased laser intensity at the pinhole, which served as a point source of light. This light was collimated by a 1 m focal length lens and the second variable aperture which passed only the zeroth order diffraction ring [5]. Two 45° quartz prisms steered the laser beam vertically and horizontally through a third stripping iris and a commercial beam
Figure 2.2 Diagram of the optics used to collimate and steer the laser through the interaction region.

reducer (Oriel model # 15620). Scattered laser light was found to be a serious problem when detecting fluorescence at the same frequency as the exciting laser pulse. To minimize this problem we used the optical system described above together with the laser at reduced power (\( \sim 1 \text{ mW} \)). In addition, all surfaces of the interaction block were sooted thoroughly. Even so, it was found that scattered light from the exciting laser pulse paralyzed the photomultiplier tube for 10 - 20 ns. Fig. 2.3 illustrates the relative beam geometries and interaction block of the apparatus.
2.2.3 The Data Collection Optics

Visible fluorescence decay radiation was collected by using an optical system consisting of three lenses in a microscope arrangement, various interference filters for wavelength selection and a photomultiplier for photo-detection. The lens arrangement consisted of a quartz plano-convex lens ($\phi = 5 cm$, $f_{l} = 7.5 cm$) placed approximately 7.5 cm from the interaction volume. A second quartz, plano-concave lens ($\phi = 5 cm$, $f_{l} = 20 cm$) and biconcave lens ($\phi = 2.5 cm$, $f_{l} = -5 cm$) were arranged together such that light collected and collimated by the first lens was reduced to approximately 1 cm in diameter. Fig. 2.4 shows the configuration of the light collection optics. The efficiency of the collection system can be calculated to be the solid angle subtended by the first
collection lens, which is about 0.08sr (i.e. $\Delta \Omega / 4 \pi \sim 0.02$). By placing a section of spherical mirror (radius of curvature = 1.9 cm) inside the interaction block, the collection efficiency is effectively doubled, yielding $\Delta \Omega / 4 \pi \sim 0.04$.

Figure 2.4 Schematic diagram of the fluorescence detection optics.

For measurements of the rotational temperature of $N_2^+$, it was important that the optical system sample only the "cold axial core" of the gas jet. This necessitated that the transmission function of the lens arrangement fall off rapidly with increasing distance from the axis of the jet. The response of the collection system is given by

$$\eta = \frac{\alpha(\theta_1) + \alpha(\theta_m)}{2}$$

(2.4)

where

$$\pi \alpha(\theta) = \theta - \sin(\theta), \cos(\theta_1/2) = (R \cdot r_2)/(2rr_1)$$
\[
\cos(\theta_{m}/2) = \frac{1}{r_1} + \frac{r_2}{2r_1} \cdot \frac{R_o}{r}
\]

and all geometric quantities are as defined in Fig. 2.5. The response curve of the detection optics is shown in Fig. 2.6. In practice, the lens arrangement was optimized using one of two methods. The first method was to insert a hypodermic needle into the interaction region, such that its tip was at the point were the electron, laser and molecular beams intersected. Since the first lens was mounted in a telescoping tube arrangement and the latter two lenses were fixed in position, the first lens was moved slowly towards the hypodermic needle until the magnified image of the needle viewed through all lenses was just out of focus. At this position the focus of the front lens coincided with the interaction volume. The second method also used the hypodermic situated in the identical position. Here, laser light was scattered off the tip and the scattered radiation collimated by the lenses and detected by a photomultiplier tube. The front lens was then adjusted for maximum signal. The two methods yielded approximately the same position for the front lens.
Detected wavelength selection was accomplished using various interference filters. Light was detected with an Amperex XP2233B photomultiplier tube in a Products for Research TE-210TSRF housing. The XP2233B is a fast (2 ns rise time
10% → 90%) high gain (3 x 10^7) tube with a S-20 photocathode for good UV response. Table 2.2 and Fig. 2.7 give a summary of the specifications of the photomultiplier tube. The housing was thermochemically cooled to about -30°C and well shielded from RF interference. At typical operating voltage of 1900 V and discriminator level of -20mV, dark counts were about 10 Hz.

![Graph showing PMT output vs Wavelength](image)

**Figure 2.7** Plot of the photomultiplier efficiency against wavelength.
Ampex XP223B photomultiplier tube
(PMT)

<table>
<thead>
<tr>
<th>Feature</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of stages</td>
<td>12</td>
</tr>
<tr>
<td>spectral sensitivity type</td>
<td>S-20</td>
</tr>
<tr>
<td>voltage for gain of 3x10&lt;sup&gt;7&lt;/sup&gt;</td>
<td>2050 V</td>
</tr>
<tr>
<td>Anode pulse rise time</td>
<td>2.0 ns</td>
</tr>
<tr>
<td>Linearity</td>
<td>up to 100mA</td>
</tr>
<tr>
<td>Window material</td>
<td>Quartz</td>
</tr>
</tbody>
</table>

Table 2.2 Summary of the characteristics of the photomultiplier tube used in this investigation.

2.3 Metastable Detection System

Measurements of the time-of-flight of metastables produced at the interaction region were carried out by inserting a metastable detector in the gas stream about 7 cm downstream from the nozzle. The detector consisted of a Galileo 4039C channeltron, a grid biased to reject positive ions and a small (φ ~ 0.5 mm) orifice to ensure only detection of gas from the coldest axial flow in the gas stream. The nosecone-orifice assembly was biased negatively to inhibit the detection of electrons by the channeltron. It was found that visually aligning the metastable detector with the axis of the valve was sufficiently accurate to ensure detection of the axial gas flow. A block schematic of the arrangement used to measure TOF spectra is shown in Fig.2.8.

A BNC pulse generator operating at 20 KHz triggered the electron beam pulser
Figure 2.8 Diagram of the metastable detector and electronics used in this investigation.
and also fed "START" pulses to the TPHC after going through an ORTEC model 934 constant fraction discriminator (CFD). The electron beam pulse width was reduced to < 0.3 μs. The signal which originated from the channeltron was handled as shown in Fig. 2.9. The signal pulses amplified by an ORTEC model 474 timing filter amplifier (TFA) and discriminated by a CFD were fed to the TPHC "STOP" input. The TPHC output was fed to the Pulse Height analyzer (PHA). The front panel of the TPHC was typically set for a 40μs time range.

![Diagram](image)

Figure 2.9 Block diagram of the electronics used to generate nitrogen metastable TOF profiles.

Spectra stored in the PHA are subsequently transferred to a computer for analysis.

### 2.4 Aspects of the Supersonic Jet Source

#### 2.4.1 The Pulsed Valve for N₂⁺ Studies

For studies involving the ionization of nitrogen, the gas beam was produced
by a Lasertechmics model LPV piezoelectrically actuated molecular beam valve. Gas from a high pressure cylinder (high purity grade) was fed to the valve through 0.25" stainless tubing and swagelok® fittings. Since the interaction block, molecular beam valve and electron gun assembly all were held at target voltage (above ground) it was necessary to electrically isolate the valve from the gas line with a Teflon spacer. Typical operating pressures at the head of the valve ranged from 15psi to 75psi. The gas handling and vacuum systems are illustrated in Fig.2.10.

When a potential difference was applied across the piezoelectric crystal bimorph, the resulting deformation of the bimorph pulled the poppet away from the nozzle. Gas passed through the flat geometry nozzle and expanded supersonically into the interaction region. The valve was typically driven with 100μs – 200μs pulses of about 100V amplitude at 30Hz. Fig. 2.11 and Fig. 2.12 illustrate the operating conditions of the LPV molecular beam valve in the experiment.
Figure 2.10 Schematic diagram of the vacuum and gas handling systems. Some details such as heater power supplies and vacuum gauges have been omitted for clarity.
Figure 2.11  Graph of the operating characteristics of the LPV piezo-electric valve for varying driving voltages.

Figure 2.12  Temporal profile of the LPV valve gas pulse. The thick line represents the driving pulse applied to the valve.
2.4.2 The Theory of Supersonic Expansion of Gases

The physical properties of a supersonic expansion have been well documented [6-8]. The expansion cools (both vibrationally and rotationally) the gas molecules. This cooling process arises from an approximately adiabatic equilibrium (isentropic) free expansion of a gas through an orifice. The expansion is at high density ($\sim 10^{13} \text{ cm}^{-3}$) and low temperature ($\sim 20 K$). A system whose temperature has been lowered has many fewer rotational and vibrational levels it can occupy, simplifying any analysis dramatically. An ideal expansion is also collision free in the jet itself, minimizing any perturbing effects which collisions between gas molecules could bring about. In simple terms the cooling arises from the conversion of random thermal motion into directed flow. The transitional velocity distribution moves from $v_x = 0$ to $v_x = v_0$. The cooling proceeds according to Maxwell's relation

$$\left( \frac{\delta T}{\delta v} \right)_s < 0$$

(2.5)

and the velocity distribution of the gas becomes [6]

$$\frac{dn}{n} = \left( \frac{m}{2\pi k T_o} \right)^{3/2} \exp \left( -\frac{m}{2k T_o} (v_x - v_o)^2 + v_y^2 + v_z^2 \right) dv_x dv_y dv_z$$

(2.6)
where $n = \text{molecular number density}$

$m = \text{molecular mass}$

$(v_x, v_y, v_z) = \text{molecular velocity parallel to the } x, y, z \text{ axis respectively}$

Following the Kantrowitz-Grey [9] treatment of a supersonic expansion, the molecular flux at some distance downstream is just the integration of the differential flux $v_x dn$ parallel to the axis over positive values of $v_x$ and all $v_y$ and $v_z$.

$$
\phi_{\parallel} = n_o \int_{v_x > 0} v_x \frac{dn}{n} = n_o \left( \frac{m}{2\pi KT_o} \right)^{\frac{1}{2}} \int_{-\infty}^\infty \exp \left( -\frac{m}{2KT_o} (v_x - v_o)^2 \right) v_x dv_x
$$

$$
= n_o \frac{1}{2\sqrt{\pi}} \left( \frac{m}{2KT_o} \right)^{-\frac{1}{2}} \exp \left( -\frac{m}{2KT_o} v_o^2 \right) + n_o v_o \left( \frac{1}{2} + \frac{1}{2} \text{erf} \left( \frac{m}{2KT_o} \right)^{\frac{1}{2}} \right)
$$

(2.7)

The flux on a plane perpendicular to $v_x$ at a distance $r$ from the centre of the expansion and a distance $l$ from the orifice is given by

$$
\phi = A \phi_{\parallel} \frac{1}{\pi l^2} \left( \frac{m}{2KT_o} \right) v_x^2 \exp \left( -\frac{m}{2KT_o} \frac{v_x^2 r^2}{l^2} \right)
$$

(2.8)

(assuming $l \gg \text{diameter of the orifice}$)

where $A$ is the area of the orifice. Integration of the flux $\phi$ over all possible values of $v_x$ yields the total flux:
\[
\phi = A_o n_o \frac{1}{\pi l^2} \frac{1}{\sqrt{\pi}} \left( \frac{m}{2KT} \right)^{\frac{3}{2}} \left( 1 + \frac{r^2}{l^2} \right)^{-2} \exp \left( \frac{-r^2 t^2}{l^2} \right) \left( \frac{\sqrt{\pi}}{2} \left( t^2 + \frac{3}{2} \right) \left( 1 + erf t \right) + \frac{1}{2} (t^2 + 1) e^{-t^2} \right)
\]

(2.9)

where

\[
l = v_o \left( 1 + \frac{r^2}{l^2} \right) \left( \frac{m}{2KT} \right)^{\frac{1}{2}}
\]

The velocity distribution of molecules on an axis is given by a combination of equations 2.7 and 2.8 with \( r \) set to zero:

\[
d\phi = A_o n_o \frac{1}{\pi l^2} \frac{1}{\sqrt{\pi}} \left( \frac{m}{2KT_o} \right)^{\frac{3}{2}} v_x^3 \exp \left( \frac{-m}{2KT} (v_x - v_o)^2 \right) dv_x \quad (2.10)
\]

For an effusive source, the equation becomes

\[
\phi_{eff} = \frac{1}{4} n_o \left( \frac{8KT_o}{\pi m} \right)^{\frac{1}{2}}
\]

(2.11)

\[
\phi = \frac{1}{4} n_o \left( \frac{8KT_o}{\pi m} \right)^{\frac{1}{2}} A_o \frac{1}{\pi l^2} \left( 1 + \frac{r^2}{l^2} \right)^{-2}
\]

(2.12)

\[
d\phi = A_o n_o \frac{1}{\pi l^2} \frac{1}{\sqrt{\pi}} \left( \frac{m}{2KT_o} \right)^{\frac{3}{2}} v_x \exp \left( \frac{-m}{2KT_o} v_x^2 \right) dv_x
\]

(2.13)

Since the average flow velocity for a thermal source is zero (i.e. \( v_o = 0 \))

Often the flow parameters for supersonic expansions are expressed in terms of the Mach number (\( M \)). The Mach number is usually expressed as the ratio of the flow velocity (\( v_o \)) to the local velocity of sound (\( a \)): 
\[ M = \frac{v_c}{\alpha} \]

where \( \alpha = \sqrt{\gamma RT} \)

\( \gamma = C_p/C_v \)

\( \gamma = 1 + 2/f \) where \( f \) is the number of degrees of freedom available to the molecule.

Using Eqn (2.9) the flow equations for the supersonic expansion become:

\[ \phi'' = n_o \alpha_o \left( \frac{1}{2} \frac{1}{\sqrt{2\pi}} e^{-\frac{(\gamma M^2)}{2}} \right)^{\frac{1}{2}} + \frac{1}{\sqrt{2\pi \gamma}} \exp \left( -\frac{\gamma M^2}{2} \right) \]  

(2.15)

\[ d\phi = A_o n_o u_o \frac{1}{\pi l^2} \left( \frac{\gamma M^2}{2} \right)^{\frac{3}{2}} \exp \left( -\frac{\gamma M^2}{2} \left( \frac{u_x}{u_o} - 1 \right)^2 \right) \left( \frac{u_x}{u_o} \right) d\left( \frac{u_x}{u_o} \right) \]  

(2.16)

For \( M > 4 \), equations (2.10) and (2.11) reduce to

\[ \phi'' = n_o u_o \]  

(2.17)

\[ \phi = A_o n_o u_o \frac{1}{\pi l^2} \left( \frac{\gamma M^2}{2} + \frac{3}{2} \right) \]  

(2.18)

The advantages of a supersonic expansion are over effusive expansions are clear from the above equations. Comparison of Equation (2.12) and (2.18) shows that nozzle sources have much higher beam intensities than effusive sources, by a factor (on axis) of
\[
\left( \frac{y M^2}{2} + \frac{3}{2} \right)
\]

The velocity distributions computed according to (2.13) and (2.16) with \( y = \frac{7}{5} \) are plotted in Fig.2.13, showing that much narrower velocity distributions are accessible with nozzle sources. Ashkenas and Sherman have given accurate fitting formulae for the variation of the centreline Mach number with axial distance:

\[
M = A \left( \frac{x - x_o}{D} \right)^{\gamma - 1}
\]

(2.19)

where \( \frac{x}{D} \) = axial distance from the nozzle orifice in orifice diameters.

Relations for the density and temperature of a perfect gas in an isentropic expansion are:
Figure 2.13  Theoretical velocity distributions for effusive and nozzle sources. From Anderson and Fenn [8].

\[
\frac{n}{n_o} = \left(1 + \frac{\gamma - 1}{2} M^2 \right)^{\frac{1}{\gamma - 1}} \quad (2.20)
\]

\[
\left( \frac{T}{T_o} \right)^{\frac{1}{\gamma}} = \left(1 + \frac{\gamma - 1}{2} M^2 \right)^{-\frac{1}{2}} \quad (2.21)
\]

where  
\[ T_o \]  the stagnation temperature of the gas  
\[ n_o \]  the stagnation density of the gas  
\[ n,T \]  the density and temperature of the gas at the Mach disc \[ M \]
Equations (2.19) and (2.21) suggest that the Mach number, and hence the temperature of the gas have no upper or lower limits respectively. In reality, the gas becomes increasingly rarefied as we follow the expansion out of the orifice. As the frequency of collisions reduces, the conversion of random thermal motion into directed kinetic energy slows and the temperature of the gas approaches some limiting value.

In practice, expansions do not take place into a region of zero pressure as assumed above because of the finite pumping capacity of the vacuum systems. The background gas at higher densities causes the jet molecules to slow down. Low background densities serve to scatter the jet molecules. For a ratio if stagnation pressure to background pressure \( P_s / P_B \) the location of the Mach disc has been found to be:

\[
\frac{X_M}{D_M} = 0.67 \left( \frac{P_s}{P_B} \right)^{\frac{1}{2}}
\]

(2.22)

Initially there is equilibrium between the rotational and translational temperatures (assuming no vibrational excitation) in the gas jet. The rotational motion quickly becomes frozen as the gas expands from the orifice as demonstrated by Marrone et al. [10] (Fig. 2.14), the freezing causing a departure from the isentropic expansion model which scales as \( P \times D \) (Torr.mm).
Figure 2.14 Plot showing the rotational temperature as a function of axial distance in a supersonic jet. (From Marrone et al.)

In essence the freezing is caused by the gas molecules in the directed flow "running out" of collisions. Models [9] have predicted that the terminal Mach number, $M_t$, for an argon expansion is given by
\[ M_r \approx 133 (P_0 D)^{0.4} \]  \hspace{1cm} (2.23)

where \( P_0 \) is the nozzle pressure in atm,
and \( D \) is the nozzle diameter in cm.

The effect of condensation also can interfere with the attainment of ultimate beam cooling. Low temperatures facilitate the formation of van der Waals dimers, which involve the release of the heat of condensation and a consequent temperature rise. It has been well documented that dimer formation depends strongly on nozzle geometry and the nozzle used in this experiment (flat geometry) is non-optimal. We also note that the process scales as \( P_0^2 / D \) [11].

2.4.3 The Pulsed Valve for CN and OH Studies

For dissociative excitation studies of CN and OH radicals a pulsed molecular beam valve was required that fulfilled certain requirements; the ability to operate at temperatures near 130\(^\circ\)C and that it be electromagnetically quiet to avoid disturbing the electron beam. The vapour pressure versus temperature of the parent molecules of CN and OH used (CH\(_3\)CN, H\(_2\)O and CH\(_3\)OH) are given in Fig.2.15.

For stagnation pressures of up to 4atm. (60psi) the valve must operate at temperatures as high as 130\(^\circ\)C. The piezoelectrically driven Lasertechnics model LPV valve used in the \( N_2^* \) studies was represented by Lasertechnics as being capable of operation at these temperatures if supplied a new crystal bimorph. This solution had the advantage of minimal modifications to the existing equipment, the new piezo-crystal bimorph was driven with the same voltage pulse characteristics,
Figure 2.15  Plot of the vapour pressure as a function of temperature for the parent molecules used in this experiment.

yielded approximately the same gas pulse profiles as the low temperature bimorph and since the LPV valve was used in the N2+ studies all mounting hardware was prepared. However, it was found that the new bimorphs were unacceptable for high temperature operation. The bimorph poppet (Fig.2.16) was discovered to be very susceptible to detachment from the bimorph at temperatures near 90°C, the epoxy used to attach the poppet to the crystal lost its integrity and the poppet would fall off.

After obtaining two replacements from Lasertechnics for bimorphs lost in this manner it was decided to attempt an in-house modification of a damaged crystal. The epoxy was removed and the poppet re-attached to the crystal with Edwards Torr-Seal® vacuum epoxy. Extreme care had to be taken to centre the poppet on
the bimorph and retain a perpendicular orientation to its surface. Tests performed on the modified crystal revealed that standard room temperature (25°C) operation was still achieved. When the valve was heated, however, a problem detected previously with the manufacturers' bimorphs became even more pronounced. When the bimorph is installed normally inside the valve body (at 25°C) the orifice is tightened until the poppet seats on the orifice. To do this, the valve is pressurized by 20 p.s.i. of N₂. "SNOOP® leak detector is placed on the orifice and the orifice assembly screwed into the valve body until very small bubbles form in the SNOOP®. However, when the valve is heated thermal expansion drives the poppet down on the orifice even harder. The vertical excursion of the poppet when a driving pulse is applied becomes insufficient to lift the poppet and the valve no longer yields gas pulses. The maximum operating temperature when the bimorph is seated in this seated in this manner was found to be about 60°C, as shown in Fig.2.17.
An attempt to solve this problem was made by first heating the valve to the expected operating temperature and then seating the poppet as above while keeping the valve hot. The valve when seated in this manner had a very narrow temperature range (~10°C) for operation. When heated too high the valve shut down and if the temperature fell the seat pulled away from the orifice and the valve leaked. The viton tip at these elevated temperatures also experienced some plasticity. The viton tip after a short length of time (approximately 48 hours at 90°C) extruded itself into the orifice due to the seating pressure. The extrusion effectively reduced the vertical excursion of the poppet assembly and the valve could not open. The viton tip was trimmed when this occurred, necessitating the complete removal and disassembly of the valve. Varying types of viton were tried to solve this problem.
When the viton was too soft the extrusion worsened, while too hard a viton required a sealing pressure which damaged the bimorph. The higher temperature also resulted in the valve having much poorer through-put than when operated at room temperature, as shown in Fig.2.17. After some time, all of these factors determined that this valve was unsatisfactory for work at elevated temperatures and was discarded.

Since an electron beam trajectory can be distorted by a magnetic field and the experiment required that electron beam energies were as low as 20eV any valve used must have low (> 30 mG) magnetic fields. It was for this reason that molecular beam valves operating with a solenoid were not at first considered for this experiment. After the LPV valve was discarded it was decided to purchase a Newport model BV-100 molecular beam valve. The BV-100 was stated to deliver 0.1ms pulses of gas at operating temperatures to 100°C and have the low magnetic fields required. The seal in the Newport valve was a viton plug pressed over the orifice by pressure applied by a "holding" solenoid. However, this viton plug was found to deteriorate rapidly at temperatures approaching 90°C in an acetonitrile enviroment and even in a dry nitrogen enviroment the plug life was typically only about 36 hours. Once the valve was removed from the interaction block mount the plug was simple to replace but the removal of the valve every two or three days was unacceptable for long-time use in the experiment and it also was discarded.

There have been many ingenious molecular beam valves reported [12-14] in the literature, but few met the design criteria noted above. A commercial car fuel
Figure 2.17 Photograph of the solenoid valve used for the CN and OH studies. The valve is shown in "exploded" form, where the length of the assembled valve is approx. 8cm. The bottom figure represents a simplified diagram of the valve body and shows the location of the magnetic field gap.
injector was chosen as the next most likely starting point for our studies. This type of valve had the advantage of being capable of operation at temperatures up to 150°C and technicians willing to attempt the necessary modifications. The valve is illustrated in Fig. 2.18. The seat in this valve was all-metal, removing the possibility of problems noted above with viton seals. Initial modifications to the valve consisted of removing the ABS plastic housing normally found around the valve, connecting a Swagelok® fitting for connection to the gas supply and grinding down the nose of the poppet. Commercial fuel injector poppets have an "hour-glass" shaped poppet end to ensure maximal dispersion of the fuel-air mixture. Since this protusion would interfere with the free expansion of gasses in this experiment, this protusion was removed. The valve was also found to already have a low magnetic field (~30 mG). Since there are no readily apparent reasons to engineer this into a car fuel injector we believe this is a fortuitous artifact of the materials and geometries used. The valve stem assembly (Fig. 2.18) which had a high residual magnetic field (~500 mG), protruded just the correct amount from the valve body which was manufactured from high permeability metal. Displacements of the valve stem by as little as 3mm yielded external fields of 60 mG. Bosch representatives were very uncommunicative as to operational or engineering specifications of the valve. The valve seat was also not "tight" enough for high vacuum operations, so to ensure a good seal at the orifice, the seat was ground with diminishing sizes of grinding compounds. The final grit size was 5μm. The valve however, as obtained from the manufacturer was found to have a design flaw for use with corrosive compounds.
The magnetic field gap (Fig.2.17) was an open pathway to the viton "o"-rings at the back of the valve. The gap was necessary to valve operation because the magnetic field circuit is completed by the valve seat as it is pulled back by the solenoid. As discussed by Mohamed et al.[16] it was found that the acetonitrile viciously attacked the viton compounds inside the valve. The viton deteriorated into small fragments which fell into the valve stem assembly, which either jammed the valve closed or inhibited the seat from closing completely. The time required for a valve to fail because of this problem was typically 1-2 weeks. An attempt to seal off the magnetic field gap with various "plastics" was attempted, but the plastic was also attacked by the hot acetonitrile. The magnetic field gap remained closed to the acetonitrile for 2-3 months and during this time the valve was opened and cleaned of plastic fragments every 3 weeks. A final design, consisting of steel for all wetted surfaces was constructed. The magnetic field gap was closed with a non-magnetic material. The valve body and stem holder were constructed out of the highest permeable alloy (SFS#43) available to the technical staff and conetic shielding was wrapped around the valve body. The spacing of the shielding was optimized empirically for minimal magnetic fields. A 500$\mu m$ orifice was placed flush with the outlet of the valve which was typically $\sim 900\mu m$ in diameter. A photograph of the valve and its operational characteristics are given in Fig.2.19 and Fig.2.20 respectively.
Figure 18 Photograph of the "all-metal" valve
Figure 2.20 (a) Graph of the "through-put" of the solenoid valve as a function of stagnation pressure for various driving voltages. In all cases the driving pulse was 0.25 ms in duration.

Figure 2.20 (b) Temporal plot of the gas jet pulse obtained using the solenoid valve. The thick line denotes the driving pulse applied to the solenoid. Profiles were obtained by monitoring e-impact fluorescence of the gas pulse.
2.5 Design and Characteristics of the Electron Optics

2.5.1 Design Criteria of the Electron Optics

It was found that in the ionizing electron impact process of $N_2 X^1 \Sigma_g^+ \rightarrow N_2 X^2 \Sigma_g^+$, secondary electrons can cause severe problems. When attempting to measure rotational temperature these secondaries cause transitions which shift the rotational populations to high rotational levels, thus "warming" the gas. These secondary electrons arise from electrons scattering from surfaces in the interaction region, or backscattered electrons from the Faraday cup. Secondary electron production can be monitored by measuring known atomic or molecular triplet excitation functions. In particular the excitation function of the $N_2 C^3 \Pi_u (v = 0) \rightarrow B^3 \Pi_g (v = 0)$ transition at 337.1 nm was used. It is known that the cross section of a triplet state from a singlet ground state is sharply peaked at low energy, and beyond the peak, decreases as $E^{-3}$ (where $E$ is the electron energy). This steep decrease can be moderated, however, by the presence of low-energy secondary electrons which can lead to additional excitation. This allowed the probing of secondary electron production. Keeping the production of secondaries to a minimum was an important factor when the electron gun was designed.

In a supersonic jet the coldest rotational and translational temperatures occur along the axis of the flow (cf Section 2.4), so another important design criterion was that the electron gun should produce a well collimated electron beam as shown in Fig.2.21. Typically most electron guns vary in magnification at the focus for different impact energies. If variations in the magnification of the lens system
causes the electron beam to expand, the overlap of the gas jet and electron beam will increase. It has been well documented that the rotational temperatures rises as a function of radial distance from the axis of the expansion. An increased overlap of the two beams therefore would then cause more of the "warmer" non-axial gas to be excited by the electron beam, causing systematic errors in the determination of rotational temperatures as a function of impact energy. When designing the electron gun it was decided that an important criterion be that its magnification remain constant with respect to varying impact energy.

![Diagram showing the overlap volumes in the triple beam experiment.](image)

Figure 2.21 Diagram showing the overlap volumes in the triple beam experiment.

To calculate the trajectories of electrons in a system of electrostatic lenses we relied upon an excellent monograph by Harting and Read [15]. An extensive treatment of all types of electrostatic lenses is given for three element electron
guns. The cardinal points of an electrostatic lens, shown in Fig. 2.22, determine the asymptotic behavior of all paraxial rays in the focusing region. By comparing similar triangles, we find,

\[
\frac{P - F_1}{f_1} = \frac{f_2}{Q - F_2}
\]

which is Newton's thick lens relationship. We can also show that the magnification is given by:

\[
M = \frac{-f_1}{P - F_1} = \frac{Q - F_2}{-f_2}
\]
In this experiment a symmetric triple element cylindrical lens stack was used as the electron focusing array. Such a three-cylinder lens had the advantage of producing an image of a fixed object at a fixed image plane, for a range of $\frac{v_2}{v_1}$. The well-known Einzel lens arrangement refers to the case where $v_1 = v_2$. For this type of lens stack where $A/D = 1.0$ and $G/D = 0.1$, Harting and Read [15] have defined a non-analytic function $F = F(v_2/v_1)$ to numerically solve for $F = f_1, f_2$ or $f_3$. A basic program written by Dr. Peter Hammond which incorporated the equations for $F$ and the necessary empirical constants was used to design the electron gun. A schematic of the electron gun is shown in Fig.2.23.
Figure 2.23  Schematic diagram of the electron gun (long variant) used.
2.5.2 The Electron Optics

The electron source consisted of a hairpin filament of throriated tungsten wire (0.005\" diameter) mounted in a ceramic holder. The electrons were extracted by a grid and anode arrangement. The grid was biased slightly (~$10V$) negative with respect to the filament. A filament current of approximately 2.3A yielded about 200\(\mu\)A of total emission current. The electron beam was pulsed by driving the potential on the cathode housing negative (~$-30V$) within about 50ns.

The electron source was imaged onto the interaction region by a single lens element. The lens voltage was typically $V_2 \approx 5V_1$. The beam was defined by window and pupil apertures separated by one lens diameter. These apertures served to collimate the electron beam. The window aperture defines the radial or angular spread of the electrons. The pupil aperture defines the pencil angle of the electron beam. The beam and pencil angles of the electron beam are defined in Fig.2.24. The pupil was placed in a field-free region ($v=v_i$), maximizing the through-put of the electron gun. Two sets of deflectors were also placed in the equipotential region which allowed minor "steering" of the electron beam. A third and final "target aperture"($\phi = 4mm$), located at the end of the electron gun served to "strip off" any halo which may surrounded the main electron beam. A second arrangement, where the apertures were approximately two lens diameters apart was also designed as a possible means of operation. This afforded a tighter pencil and beam angle, which was thought to be important to keep the warmer regions of the expansion unexcited. The calculated characteristics of both electron guns are
given Fig. 2.25 and Fig. 2.26. In practice the long variant of the electron gun yielded 1/2 of the current of the short variant as recorded on the inner faraday cup. The ratio of inner to outer faraday cup currents in both variants was typically 10:1, and rotational distributions in ionized nitrogen (Section 3) were identical to within experimental accuracy. In most cases the short variant was used in data collection.

Figure 2.24 Ray diagram which defines the beam and pencil angles for a beam passing through a pair of apertures.

Figure 2.25 Plots showing the magnification, beam and pencil angles as a function of lens potentials for the “long” variant of the electron gun.
Figure 2.26 Plots showing the magnification, beam and pencil angles as a function of lens potentials for the "short" variant of the electron gun.

The electron gun was mounted on an aluminum block which is at target potential. The block had various holes machined into it to allow for the observation of fluorescence, passage of the electron and laser beams and the expansion of the gas jet. The electron beam after passing through the interaction region was collected in a Faraday cup especially designed to minimize backscattered electrons. The Faraday cup as shown in Fig.2.27 had a repeller field built into its design. The resulting field served to confine any scattered low energy electrons to the long (∼ 4") Faraday cup. Typically the repeller was operated at -30 Volts with respect to target potential. The end of the Faraday cup consisted of two smaller (ϕ = 4 mm, ϕ = 8 mm) inner Faraday cups, insulated from each other. The "small" and "medium" Faraday cups were biased positively about 50 to 30 V with respect to target respectively. In this way currents were monitored at the anode, target aperture, interaction block, Faraday cup body, medium Faraday cup
body, medium Faraday cup and small Faraday cup. Typically the electron beam was very well collimated, with a small Faraday cup to Faraday cup body current ratio of 10:1.

![Diagram of Faraday cup and repeller electrodes]

Figure 2.27 Schematic diagram of the Faraday cup and repeller electrodes.

We could readily find focusing conditions where secondary electrons were produced in significant quantities. Fig.2.28 shows a plot of the excitation function of the $N_2 \quad C^3 \Pi_u (\nu = 0) \rightarrow B^3 \Pi_u (\nu = 0)$ transition with varying electron impact energy. The production of secondaries was evidenced by a slower drop of the cross section as $E$ was increased. Under these conditions significant warming of the LIF spectra was observed as shown in Fig.2.29.
Figure 2.28 Excitation function of the N$_2$ C-B transition as a function of electron-impact energy. Open triangles are the data of Aarts et al. [17], squares represent the data of Jobe et al., which the data is normalized to. The solid and broken curves represent focusing modes of the electron gun which produced minimal and significant quantities of secondary electrons, respectively.
Figure 2.29 Rotational LIF spectra of the $\text{N}_2^+$ B-X transition after electron impact ionization. The top figure represents a spectra obtained with minimal secondary electron production. The bottom curve represents a spectra obtained with a significant amount of secondaries being produced. Both spectra were obtained for a stagnation pressure of 3 atm. Note the enhancement of the high $N^*$ lines.
2.6 **Electronics**

2.6.1 **Triple Beam Timing Electronics for N$_2^+$ Studies**

This experiment required accurate timing for the gas jet, electron beam and laser beam. To achieve this a master oscillator (repetition rate from 0.1 Hz to 1 KHz) with three channels of variable delay outputs (delay times from 1µs to 1ms) was used. One of these outputs went to each of the molecular beam driver, cathode housing pulser, and an ORTEC model 416A gate and delay generator (which was connected to the N$_2$ laser pulsing unit). In this way the relative timing between the electron beam and laser beam could be selected to within 10ns. A block schematic of the timing arrangement is shown in Fig. 2.30.

![Block schematic of the timing electronics](image)

**Figure 2.30** Block schematic of the timing electronics used in the nitrogen experiments.

A home-built molecular beam valve driver supplying pulses of 70-120 V amplitude was used. The output pulse was not referenced to ground, but to the electron target potential. A time delay of $\approx 200\mu$s existed between the driving
pulse being applied to the valve, and the onset of the gas pulse. This was due to the characteristic response time of the crystal bimorph inside the molecular beam valve, which can be seen in Fig. 2.12.

The electron beam was pulsed by varying the voltage applied to the cathode housing. Typically the "best" focusing of the electron beam was achieved with a 5V to 10V negative (with respect to ground) potential applied to the cathode housing. To turn off the electron beam a large repelling field of 40V to 50V negative (with respect to ground) potential was applied on the cathode housing. A temporal profile of the cathode housing pulse is shown in Fig.2.31. The trailing edge of the pulse had a fall time of 50 ns (half-maximum). The width of the cathode housing pulse and therefore the electron beam could be varied continuously between 8 ms and 0.4 μs. The electron beam pulser had four modes of operation: DC/ON, DC/OFF, Pulsed/Normally ON and Pulsed/Normally OFF.

Radio-frequency noise from the nitrogen laser was prevented from reaching the counting electronics by inserting a fibre optic link between the nitrogen laser and the timing electronics. By doing this, the counting circuitry could be started closer in time to the laser pulse, before excited ions or metastables could drift out of the field of view or before the spontaneous fluorescence emission from the laser-excited levels had decayed significantly.

The timing relationship between the three beams was set typically as follows: First, a temporal profile of the gas pulse from the molecular beam valve was measured. The electron beam pulser was set to the DC/ON mode of operation
Figure 2.31 Temporal plot of the grid pulse and resulting fluorescence from the N₂ B-X emission.

and the electron beam set about 2μ A DC, and somewhere in energy above the threshold of the fluorescing level to be observed. The low electron beam current ensured that the photomultiplier would not be saturated by the direct fluorescence. The molecular beam valve was connected to channel 1 of the master oscillator, the delay set to 0.001 μs and the pulse width to about 100 μs. A suitable interference filter was selected to observe the direct fluorescence from the electron-excited ions created in the gas jet. Typically this was either the 3900 Å or 4300 Å filters for the N₂⁺ B-X (ν' = 0, ν'' = 0) or N₂⁺ B-X (ν' = 0, ν'' = 1) transitions respectively. Output from the photomultiplier was connected to an ORTEC model 474 timing filter amplifier (TFA), whose output was connected to one input of a two input AND logic gate in a Le Croy model #365-AL unit. The other input of the AND gate was connected to channel 2 of the master oscillator. The AND gate was set for a 50ns
width and its output connected to an ORTEC model 775 counter. The counter was gated ON by an ORTEC model 719 timer (typically for 30 seconds). The delay of channel 2 (essentially the location in time of the counting gate) was advanced from 0 \mu s to 999 \mu s in steps of 5 - 10 \mu s, and the counter initiated after each advance. The delay time and corresponding counts of direct fluorescence were then recorded. The electron beam pulser trigger input was then connected to channel 2 of the master oscillator and the delay set such that the electron-beam would intersect the peak of the gas pulse. The ORTEC gate and delay generator was then connected to channel 3 of the master oscillator and the delay set approximately that of the electron beam. The output of the TFA was then connected to an oscilloscope, the electron beam pulser set to the "Pulsed/Normally OFF" mode of operation and the laser started firing. The laser pulse as seen by the PMT could then be viewed on the oscilloscope and adjusted in time using the Vernier scale on the ORTEC delay generator to the desired delay after the termination of the electron beam.

2.6.2 Data Collection Electronics for \text{N}_2^+ Spectra

A block schematic of the electronics used to generate LIF spectra is shown in Fig. 2.32.

Signals from a photodiode were fed to an EG\&G model T105/N fast (750MHz) discriminator. An output from the discriminator fed the "START" input of an ORTEC model 467 time-to-pulse height converter (TPHC). Another output from the discriminator was connected to an ORTEC model DB463 variable delay box,
Figure 2.32 Block schematic of the electronics used to generate rotational spectra in the nitrogen studies.

The resulting delayed pulse was reshaped by a LeCroy model #365AL logic unit to be up to 50ns in duration, and then fed to one input of an AND gate in the LeCroy logic unit. The other input of the AND gate was fed signals from the photomultiplier, and was amplified and conditioned by a TFA-CFD pair. The output of the AND gate was connected to the "STOP" input of the TPHC. In this way the TPHC was being utilized as a coincidence gate. The gate width was determined by the TPHC range on the front panel which was set to be of the same order as the fluorescence decay lifetime of the laser-excited level. The LeCroy AND gate ensured that "STOP" pulses at the TPHC originated from fluorescence observed after allowing the photomultiplier to recover from the scattered laser light. "TRUE STOP" pulses from the TPHC which signalled the observance of a fluorescence photon within the coincidence gate, were fed to the input of a multichannel scaler (MCS). Signal rates were sufficiently low so that pile-up error in the TPHC was negligible. The (MCS) channel advance was driven by the stepper motor controller to the dye laser. Since the stepper motor driver was not electrically isolated from radio-frequency pickup from the nitrogen laser, it was necessary to insert an optical
isolation stage between it and the stepper motor driver. A divide-by-$2^m$ prescaler circuit was also added to allow larger spectral scans from the stepper motor controller (by $2^m$).

A spectral scan was set up by the following relationship

$$\Delta \lambda = \frac{N_{\text{int}}}{12.5 \times n_L}$$

where $\Delta \lambda$ is the width of the scan in angstroms,

$n_L$ is the order in which the dye laser grating is operating,

and $N_{\text{int}}$ is the number of pulses sent to the stepper motor

(set by the user on the front panel of the stepper motor driver)

The necessary number of channels to contain the spectral scan in the MCA memory was

$$M = \frac{N_{\text{int}}}{2^m}$$

(2.)

where $M$ is the number of channels in the MCA and $2^m$ is the preset scaling factor ($m = 0.5$). If the number of channels were too large, the scaling factor need only be increased.
2.6.3 Data Collection Electronics for N₂⁺ LIF-TOF Studies

A block schematic of the electronics used to collect LIF-time-of-flight profiles is shown in Fig. 2.33.

![Block schematic of the electronics used to generate the LIF--TOF profiles in the nitrogen experiments.](image)

Figure 2.33  Block schematic of the electronics used to generate the LIF--TOF profiles in the nitrogen experiments.

It is worth noting at this point that this TOF technique was rotational state selective, and the technique was unique to this study. The heart of the apparatus was a special interaction region where for these studies the probing laser beam was displaced 1 cm downstream (of the expansion) from the electron beam axis. Output from the photomultiplier was routed through a TFA and CFD (-2V pulses, ~5 ns width), then to one input of an AND gate in a LeCroy logic unit. Laser pulses detected by the photodiode were delayed 80 ns, to avoid data accumulation in a temporal region where the photomultiplier detects scattered laser light. The photodiode pulse then was lengthened to approximately 50 ns in width and fed to the second input on the
LeCroy AND gate. The output from the AND gate was fed to the "STOP" input on the TPHC. "START" pulses for the TPHC were taken from the discriminated output of the BNC clock unit for the electron beam pulser. The TPHC was set (via the front panel time range adjustment) for a coincidence gate of about 40 $\mu$s. By the laser remaining stationary in time, the electron-beam randomly sampling the gas jet at 20 KHz and the time between electron beam pulse and fluorescence photon being recorded, a TOF profile could be collected.

2.6.4 Data Collection: Electronics for CN and OH Studies

The coincidence gate scheme (cf Section 2.5.1) composed of a TPHC and a MCS was limited to detecting only one possible fluorescence photon per laser pulse. This was due to the dead time of the TPHC ($\sim 1 \mu s$) and the presence of only one "START" pulse for every laser shot. Additional fluorescence photons detected by the photomultiplier from the laser excited state molecules were ignored by the counting electronics. For the generation of CN and OH LIF rotational spectra a Stanford Research Instruments model SR400 photon counter replaced the TPHC and associated electronics. Under some conditions the use of the photon counter increased the fluorescence detected to 4 counts per laser shot, although typically this was 1.5 counts per laser shot. The photon counter had programmable gate variables, a 200MHz counting rate, a 5ns pulse pa'ter resolution and discriminator range of -300mV to 300mV on the rising or falling edge. The photon counter was interfaced to an IBM XT (operating at 8MHz) over the RS232 serial port. A program written in 8086 assembly language and Fortran 87 accepted data from the
photon counter, displayed them on the screen, and allowed for changing the gate settings from the computer keyboard. The program also communicated over the parallel port to the dye laser stepper motor controller. A successive program written entirely in Turbo Pascal enabled radiative lifetimes and cross sections measurements to be carried out. The technique used to set-up the photon counter for optimum operation is given in Appendix A.

In order to collect LIF-TOF spectra for OH and CN the electronics used in the nitrogen LIF-TOF studies was deemed unwieldy and a new apparatus was used. Time-of-flight measurements were obtained using interaction regions with an offset between the exciting electron-beam axis and the probing laser-beam axis. For these investigations a number of new interaction blocks were made, such that the available offsets were now 0.5cm, 1.0cm and 1.5cm. Also a digital delay generator was inserted into the triggering electronics for the laser system. The in-house built delay generator was connected to the computer controlling data acquisition so that a program running on the computer could ramp the trigger delay to the pump laser. To collect a LIF-TOF profile the exciting electron beam would be set to a pulse width of >0.3 μs and such that it intersected the "peak" of the gas jet. The data collection program would then trigger the laser (with zero delay between electron-beam and laser-beam) and accumulate the fluorescence signal over a specified gate width for 200-300 laser pulses. The computer would then increment the trigger delay to the laser and start data accumulation again. At the end of a specified number of delay steps, the trigger delay would be reset to zero and the
process restarted.

2.7 REFERENCES


SECTION 3

ROTATIONALLY RESOLVED ELECTRON IMPACT IONIZATION OF N₂

IN A SUPERSONIC JET

3.1 Introduction

The use of supersonic expansions has been rather extensive during the last 20 years in almost all areas of spectroscopy and the electron-impact excitation of these molecular beams has also been an area of considerable interest. The unsophisticated systems resulting from the cooling in the jet allow simplified theoretical modeling of the interactions. The most studied collision partner in these investigations has become the nitrogen molecule due to its relatively high cross section (17.4 x 10⁻¹⁸ cm² at 100 eV) [43] for electron impact excitation to the B²Σ⁺ state and an open (0.1 nm) rotational structure for the B²Σ⁺ → X²Σ⁰ transition at 391.4 nm. The first to probe the rotational temperature of a flowing gas was Muntz [1], who used electron excitation of the B-X emission of nitrogen. At that time the process was modeled using the known oscillator strengths and dipole selection rules to describe the excitation by 10 keV electrons. However, two investigations by Talbot [2] and Marrone [3] demonstrated that there were serious deviations from the emission spectra predicted by dipole excitation theory. The higher rotational levels, characterized by the rotational quantum number N, were more populated than theory predicted. There were two general explanations of the anomalously warmer rotational populations. Muntz [1] assumed for the dipole model that the neutral N₂ level populations were distributed according to Boltzmann statistics. The first explanation was forwarded by Marrone [3] where it was correctly stated that
there is no reason to expect the ground state neutral \textit{N}_2 in rapid expansion to have rotational populations distributed according to Boltzmann statistics. Polanyi and Woodal [4] and Bassi et al [5] have stated that the probability of rotational to translational energy transfer decreases with increasing \textit{N}. This behavior would cause the cooling of higher-\textit{N} rotational levels to lag behind the low-\textit{N} levels. Recent experimental work [5-9] has supported this theory.

In the second argument it was stated by Ashkenas [10] that the anomalous population of high-\textit{N} states by electron-impact excitation persists for cold nitrogen under equilibrium conditions. This implies that the dipole excitation model may be insufficient, requiring higher order transitions to account for the anomalous population distributions. For electron impact energies of keV it is not clear what could cause these higher order transitions because the process should be almost perfectly described by the Bethe approximation [11]. If there were low-energy secondary electrons present in these past studies, collisionally induced transitions from the ground state neutral \textit{N}_2 have been suggested as an explanation of the perturbed distributions [12-15]. Sukhin and Sharafutdinov [12] have made use of the fact that the relative contribution from secondary electrons increase with radical distance from the primary beam, in order to calculate transition probabilities for \( | \Delta \textit{N} > 1 | \). Higher order transitions have also been suggested by Kassem and Hickman [16] and Coe et al. [17] as occurring due to the ejected electron and ion interacting. Coe et al. [17] suggested that the initial dipole excitations comes from the primary electron while one or more quadrupole interactions probably occur with ejected electron. Secondary electron production scales with gas
density and Coe et al. [17] found the "warming" trend did not scale until a critical
density of $10^{14}$ cm$^3$ was reached. Since the low gas density spectra still exhibited the
warming effect, the ion-ejected electron model was rejected.

The warming trend was observed in most subsequent studies involving
electron-excited $N_2$ and $N_2^+$ analysis [18-23]. The variation with electron impact energy
has been of most interest. DeKoven et al. [19] found, as most others have, that the
intensities in the tail of the distribution increase with decreasing electron energy.
Following the arguments of Coe et al.[17], the ejected electron distribution peaks at
lower energies as the incident primary electron energy is decreased. This causes a
greater probability for optically forbidden transitions to occur. This may occur, as
Hernandez et al.[22] pointed out, because at lower primary electron impact energies
the optically forbidden transitions may occur because of the increasing significance of
higher-order multipole transitions within the Born approximation [24], or a breakdown
of the Born approximation itself. Hernandez et al.[22] found that for impact energies
below $E = 800$ eV, $|\Delta N| = 3$ transitions became important. They also found that for
impact energies $E \leq 100$ eV, higher order transitions became significant. In another
investigation Becker et al.[23] showed that a reduction in incident electron energy from
600 eV to 35 eV resulted in a warming effect observable as a 35% broadening of the
intensity profile for $N_2$ $C^1 \Sigma_u^+ \rightarrow X^1 \Sigma_g^+$ (0-0) emission. Again the non-Boltzmann
rotational distribution was observed. Whereas Coe et al.[17] suggested an electron-ion
interaction as responsible for warming, there was no such pair in the study by Becker
et al.[23] who observed emission spectra in neutral $N_2$. 
A tunable dye laser provides a very useful tool to probe the rotational level population distributions. The first to use this technique was Allison et al. [25] who probed the $N_2^+ X^2 \Sigma^+_g$ ground state population distribution in a static gas cell at room temperature. They found that the rotational levels of the vibrational $v=0$ state followed a Boltzmann distribution whose temperature was found to increase very weakly with electron impact energy over the range 60eV to 100eV. The magnitude of their error made it difficult to quantify the effect. Similar laser-induced fluorescence (LIF) studies have been performed by Lester et al. [26], Helvajian et al. [27], Kondow et al. [28] and Nagata et al. [29]. Lester et al. observed only minimal warming as their electron beam energy was reduced from 80eV (31.3K) to 50 eV (37.6K). Temperatures were extracted from the spectra by fitting the first six rotational lines to a so-called "Boltzmann" plot. Helvajian et al. measured $N_2 X^2 \Sigma^+_g$ ground state populations at one energy (300eV) and made the further questionable assumption that, because of the similarity of their observed spectra to those of Lister et al, the measured distribution was insensitive to electron energy. They were, however able to measure $N_2 X^1 \Sigma^+_g$ neutral ground state rotational populations directly, using two-photon excitation of the Lyman-Birge-Hopfield bands $(X^1 \Sigma^+_g - A^1 \Pi_g)$. Kondow et al. observed a fairly substantial rotational warming (an increase of rotational energies of 35%) as the impact energy was reduced from 100 to 35eV. Nagata et al, extending the work of Kondow et al, found the average rotational energy increased from 2.26 meV to 4.24 meV as the impact energy was lowered from 300 eV to 25 eV. Secondary electron processes were clearly identified in these studies.
In the present study we probe, by means of LIF, the $N_2 X^2 \Sigma_g^+$ ionic ground state rotational level populations which have been produced by electron-impact excitation of a supersonic jet of $N_2$. We also are able to measure the translational energy of both the $N_2^+$ and $N_2$ neutral molecules by applying time-of-flight (TOF) techniques. We concentrate mostly on the variation of populations with electron energy and the influence of secondary effects.

3.2 Theory

The first attempted explanation of the $N_2^+$ B-X(0-0) electron-impact excitation emission in terms of a dipole excitation model was by Muntz [1]. He assumed the optical excitation process approximated the electron impact ionization-excitation process. Here the dipole selection rules of $|\Delta J| = 0, 1$ regulated the system as depicted Fig.3.1. For both the neutral and ionized nitrogen molecule, all states are fully described by Hund's coupling case B [30], where the electronic spin is weakly coupled to the internuclear axis.
Figure 3.1 The excitation scheme of Muntz.

Since the selection rules for electron excitation demand that transitions cannot occur between ortho and para levels of a homonuclear molecule, therefore the symmetry selection rule that $\alpha \leftrightarrow s$ is still valid in the case of ionization. Any model which is formulated to describe the ionization process must therefore contain only transitions of $\Delta J = odd$. In the case of this investigation where ground state ions are being produced Fig. 3.4, it must be required that $\Delta J = even$ transitions are only possible. Helvajian et al. [27]. did not appear to consider this when reducing their data, since they used the excitation model of Coe et al. [17]. which is valid only for $\Delta J = odd$. 
The fluorescence intensity of a rotational level \( J \) in emission is

\[
I_J = A S_J C_J(T) \exp\left(\frac{-\Theta J(J+1)}{T}\right)
\]  \hspace{1cm} (3.1)

where

- \( C_J \) is a constant describing the arrangement of the rotational population during the excitation.
- \( A \) is a constant independent of rotational temperature \( T \), which includes the Franck-Condon factor and the electronic term transition matrix element,
- \( S_J \) is the appropriate Hoenl-London factor for P or R branch emission and
where \( \Theta \) is the rotational constant for ground state \( \text{N}_2 \) (\( v = 0 \)) in degrees Kelvin. For an \( R \) branch transition in emission in a \( \Sigma^2 - \Sigma^2 \) system the Hoenl-London factor is \( 2J(J + 1) \).

Muntz [1] assumed in equation (3.1), that the target rotational level populations were described by a Boltzmann distribution, and that the contribution to the excitation from ground state \( \text{N}_2 \) vibrational levels \( v > 0 \) was negligible. For a supersonic expansion, the interaction region is approximately collision free. Many investigations have shown that the population distribution of the rotational levels is non-Boltzmann for large \( J \). In an experiment involving \( I_2 \), it was demonstrated that the rotational level populations can be described as a Boltzmann distribution up to \( J = 6 \). Helvajian et al. in an experiment with supersonically cooled \( \text{N}_2 \) found that the populations could be described out to \( J = 3 \) as a Boltzmann distribution with \( T = 10 \text{ K} \). The latter assumption by Muntz is valid for \( T_{res} < 800 \text{ K} \), where \( T_{res} = \) reservoir temperature. At this temperature the vibrational population of the \( v = 1 \) state is only about 1\% of the \( v = 0 \) vibrational state population.

It is from equation (3.1) that one can extract a so-called "Boltzmann plot", to obtain the rotational temperature. The slope of a line plotted as \( \ln \left( \frac{I_J}{\bar{I}_J} \right) \) versus \( J(J + 1) \) yields the rotational temperature directly. In our case the temperature dependent term \( C_J(T) \) complicates the evaluation, but a measure of the linearity of \( \ln \left( \frac{I_J}{\bar{I}_J C_J(T)} \right) \) versus \( J(J + 1) \) still shows the quality of fit.

We assume a dye laser pulse can be represented as a rectangular pulse of duration \( \tau \), and that the LIF signals arise from the spontaneous emission of radiation detected
after the laser pulse fully terminates. In a two level system we define the upper state and lower state populations to be denoted by \( n' \) and \( n'' \) respectively. The time-varying populations then can be written as

\[
\frac{\delta n'}{\delta t} = n'' \rho B_a - n'(A + \rho B_a)
\]

(3.2)

where \( \rho \) = radiation density of the exciting laser pulse, and \( B_a, B_s \) and \( A \) are the Einstein coefficients. We can write then for the time during the laser pulse (\( t < \tau \))

\[
n'(t) = n'' \rho B_a(A + \rho(B_s + B_a))^{-1} \times (1 - \exp(-(A + \rho(B_s + B_a))t))
\]

(3.3)

where \( n'' = n' + n'' \). After the laser pulse terminates, if no alternate decay paths from the excited state population \( n'(t) \) are possible (eg. quenching), then the intensity of the fluorescence signal \( I \) can be described by

\[
I \propto n' \frac{B_a}{B_a + B_s}
\]

(3.4)

and since \( \frac{B_s}{B_a} = \frac{g''}{g} \)

\[
I \propto n' \frac{g'}{g' + g''}
\]

(3.5)

if the laser saturates the upper state. The Einstein coefficient in absorption can be written as
\[ B_a = \left( \frac{8 \pi^3}{3 \hbar^2 c} \right) L_{J'J'} \left( 2J' - 1 \right) \] (3.6)

where \( L_{J'} \) is the appropriate line strength for the transition.

### 3.3 Results and Discussion

The experimental apparatus has been discussed above [cf Section 2], but some salient points should be made here. Over the wavelength region used to collect rotational LIF spectra, the dye laser power was monitored to be approx. constant (± 2%) and any pulse-to-pulse fluctuations in intensity were averaged out over the collection time. The interference filter used had a spectral transmission roughly rectangular in shape, centered at 390nm with a 10nm bandpass. We do not expect any distortion of the spectra because of either the filter or dye-laser specifications. Dye laser intensity was kept in the linear absorption regime for all investigations presented below.

Measurements of the translational energy of the ionized nitrogen were carried out using an interaction block where the laser beam axis was displaced 1cm downstream (of the expansion) from the electron beam axis (cf Section 2.6.3)

LIF spectra of the transition \( N_2^+ \ X^2 \Sigma_g^+ (v = 0) \) to \( B^2 \Sigma_u^+ (v = 0) \) were obtained for various energies and a wide range of operating parameters. We found that the elimination of the contribution of secondary electrons to the excitation is crucial to ensuring that the observed rotational distribution characterizes the nascent ground state ion (cf Section 2.5.2). Great pains were taken in the design of our apparatus
to ensure that secondary effects were minimized, in particular a relatively open interaction region was constructed to eliminate electron scatter from the surfaces and an repelling field was employed at the Faraday cup entrance to stop backscattered electrons. As well as this, the secondary electron contribution could be monitored by measuring known atomic or molecular triplet excitation functions, for example, the excitation function of the \( N_2^+ \, C^3 \Pi_u \ (v = 0) \) to \( B^3 \Pi_g \ (v = 0) \) transition at 337.1 nm (Fig 2.28). It is known that the cross section for the electron excitation of a triplet state from a singlet ground state is sharply peaked at low energy and, beyond the peak, decreases like \( E^3 \) where \( E \) is the impact energy. This steep decrease can be moderated, however by the presence of low energy secondary electrons which can lead to additional excitation. This allowed us to probe for the contribution of secondaries.

Fig. 3.3 and Fig 3.4 illustrate typical LIF spectra. Fig. 3.3 represents the \( N_2^+ \) (X,\( v = 0 \)) state probed by the laser with a head pressure of 3 atm and an electron impact energy of 50 eV. Fig. 3.4 represents LIF spectra obtained at three different head pressures and at two different incident electron energies, 80 and 300 eV. These data were obtained using a 1 \( \mu s \) delay between the end of the laser probe pulse. Data taken with the laser probe occurring during the electron pulse are similar but showed slightly more enhancement of higher rotational lines. Two facts are clear from Fig. 3.4. First, rotational development (temperature) decreases as the stagnation pressure behind the supersonic nozzle is increased and second, the data taken at two different energies are very similar in each case. Measurements taken at incident electron energies below 80
Figure 3.3  Rotational LIF spectra of the $\text{N}_2^+$ (B-X) transition obtained at 3 atm stagnation pressure with an impact energy of 50eV. Laser probe introduced 1 $\mu$s after termination of electron beam.
Figure 3.4  Rotational LIF spectra of the $N_2^+$ (B-X) transition obtained at different electron-impact energies under various gas beam conditions. Laser probe introduced 1 μs after termination of electron beam. The three top spectra were taken at 300eV while the three bottom at 80eV impact-energy. Pairs of spectra (a), (b) and (c) were obtained for stagnation pressures of 2, 3 and 5 atmospheres, respectively.
eV indicate that a slight warming trend does occur at these lower energies. This is discussed further below. We note that on the data taken at 4 atm driving pressure there is essentially no rotational development beyond R(4) indicating that only the first few rotational levels are being populated. This is in contrast to much of the data reported in the literature where much higher rotational development is observed. Our finding of a slight cooling after the electron beam is switched off is also in direct contrast to the findings of Nagata et al.[29] who report a warming trend which increases with time after the electron pulse is terminated.

We could readily find beam focusing conditions where secondary electrons were produced in significant quantities, as evidenced by a slower drop of the cross section as E was increased. Under these conditions significant warming of the LIF spectra was observed. We also found evidence to suggest that a variation in rotational temperature across the supersonic jet occurred, the coldest region being in the very centre. Comparison of Fig. 3.4 with Fig.3.5 illustrate two examples of spectra with much greater excitation of higher rotational levels caused by secondary electrons from the front aperture of the electron gun (Fig.3.5 [a]) and by non-optimal focussing respectively (Fig.3.5 [b]). By using the specially designed electron gun in which the magnification was kept constant as a function of impact energy, and by using light collection optics with a rather small depth of field, we were able to limit our excitation-observation region to a small volume on the axis of the jet and in this way minimize experimental warming effects.
Figure 3.5 Rotational LIF spectra of the $N_2^+$ (B-X) transition for different experimental conditions which enhance "warming" of the rotational temperature. (a) was obtained using $\sim 50\mu A$ of electron beam current on the last aperture of the e-gun. 3.5 (b) was obtained using an electron beam that was un-focused at the interaction region.
Fig. 3.6 illustrates the 2, 3 and 4 atm data reduced to so-called Boltzmann plots on which a straight line represents a Boltzmann distribution whose temperature is obtained from the slope [30]. The ionic rotational population is clearly non-Boltzmann and there is some enhancement of even rotational levels. A best-fit straight line through the data points for rotational levels $N = 0$ to 3 yielded a temperature of approximately 14 K for the 4 atm data. This may be compared with temperatures for the 3 and 2 atm data, obtained in the same way, of approximately 17 and 22 K respectively.

In addition to the warming effect (noted above) of stray low-energy secondary electrons there are other secondary processes (which could lead to rotational relaxation among the ground state ions). Various collision processes, ion-neutral and ion-ion, could occur in the still expanding jet. The process involving ion-ion interactions in the gas sample bears discussion. Because of the relatively concentrated supersonic beam ($= 10^{15} - 10^{16} \text{ cm}^{-3}$) we expect ground state ion densities of the order of $10^{11} \text{ cm}^3$ possibly leading to significant ion space charge effects.

Recent drift tube experiments [31] indicate substantial field-induced rotational heating for $N_2^+$ in fields of 5 V cm$^{-1}$. There is also the evidence of Erman et al. [32] that $N_2^+ B^2 \Sigma_u^+$ state lifetimes, measured in a supersonic jet, decrease by $\approx 13\%$, as the rotational number, $N$ approaches zero. They attribute this shortening to the rotational quenching brought about by the Coulomb repulsion.
Figure 3.6 Boltzmann plots of the level populations extracted from the spectra in Fig. 3.4. (a), (b), and (c) are obtained for stagnation pressures of 2, 3, and 4 atm, respectively. Solid line shows the results of three 300 eV open points 80 eV data. The error bars shown in (c) are representative of the errors for the data in (a) and (b).
Figure 3.7  Rotational level populations extracted from the LIF spectra taken under conditions similar to those in Figure 3.4 (c). The data represents an average of a number of spectra and of both P and R branches of the spectra. The solid curve represents a 10 K Boltzmann distribution characteristic of the ground state neutral N₂ (see text). The dashed curve represents a 14 K Boltzmann distribution.
Fig. 3.7 shows the rotational level populations obtained using a number of spectra obtained under conditions identical to those in Fig. 3.4. Both R and P branches of the spectra were used in conjunction with the relation [30]

\[ n_N = C(\Omega) I_{UF} \frac{2N + 1}{S_N g} \]  

(3.7)

where \( n_N \) is the rotational level population of the level \( N \) of the \( N^1 \Sigma^+_g \) \((v=0)\) state, \( C(\Omega) \) is a term which depends only weakly on the transition frequency \( \Omega \) and includes the transition moment, the Franck-Condon factor and geometrical factors. \( I_{UF} \) is the integrated intensity of the \( \text{Li}^+ P2 \) peak, \( 2N + 1 \) gives the rotational level degeneracy. \( S_N \) is the Hoenl-London line strength for the P or R branch of the spectrum, \( S_N^p = N, S_N^r = N + 1 \), and \( g \) is the nuclear spin degeneracy, \( g = 2 \) for \( N \) even, \( g = 1 \) for \( N \) odd.

Again no clear difference in the population distribution for the two impact energies is evident. The solid curve in Fig. 3.7 represents a Boltzmann distribution of temperature 10K which we obtained from TOF spectra as discussed below. The dotted curve represents a Boltzmann distribution of 14 K which seems to give a reasonable fit to the data points.

If we assume that equilibrium between rotational and translational motion has been established in the supersonic expansion, then an estimate of the "temperature" of the target \( \text{N}_2 \) can be obtained from measurements of either its rotational or translational temperature. Helvajian et al. [27] found a rotational temperature of 10K in a supersonic \( \text{N}_2 \) beam by directly probing the \( X^1 \Sigma^+_g - A^1 \Pi \) transition. Hernandez
et al.[21] deduced a temperature of 9.7 K for their cooled N₂ beam using high energy electron impact and direct fluorescence from N₂⁺, B²Σ⁺. We were able to gain information about the transitional temperatures of our N₂⁺ molecules by performing time-of-flight (TOF) measurements as discussed earlier.

For the neutral molecules we used the N₂ metastables produced in the interaction region as the probe and the N₂⁺ ions we monitored directly using the displaced laser probe as discussed earlier. The TOF data were fitted using a velocity distribution of the type [33]

\[ f(\nu) = \nu^n \exp \left( -\frac{m(\nu - \nu_s)^2}{2kT} \right) \]  

(3.8)

which describes a Maxwell-Boltzmann velocity distribution characterized by a temperature T, superimposed on the stream velocity \( \nu_s \) for flux (n=3) or number density (n=2). The only free parameter in the fit was the temperature since the flow velocity, \( \nu_s \), is related to T at the peak velocity, \( \nu_p \), of the measured distribution by

\[ \nu_p(\nu_p - \nu_s) = \frac{n k T}{m} \]  

(3.9)

An N₂ metastable TOF spectrum is shown in Fig.3.8. To obtain the spectrum the electron pulse was reduced in width to less than 0.3 μs. TOF spectra were obtained for a range of energies, 25-300 eV, and no significant variation in the temperature or the quality of fit was observed. We therefore believe that the metastable velocity distributions are not distorted by kinematic effects as discussed, for example by Pearl et al. [34]. The temperature derived from the TOF data is indicative of the temperature
of the ground state N$_2$ gas at the interaction region. This is strictly true if interactions among the metastables en route to the detector are negligible. In order to enforce this we rely on strong collimation at the detector (entrance collimation ratio of 60:1). Collisional energy transfer which would tend to cool the metastables further would also knock them out of the solid angle of detection. Fig.3.10 indicates that the fit of our data to the theoretical TOF spectrum, which is calculated under the assumption of undisturbed flight to the detector, is good. Deviations from the calculated distribution on the high-velocity side are probably due to metastables produced in the shock wave region surrounding the cold core of the expansion [35].

Figure 3.8  Nitrogen metastable TOF spectrum. The solid line is a theoretical distribution (equation 3.8 with n=2) with T=10K.
The measured temperature of 10 K is high compared to that predicted by ideal isentropic expansion but agrees with the temperature obtained from the N$_2^+$ TOF data as can be seen from Fig.3.9. The reason for this slightly elevated temperature may be partly due to non-ideal operation of the valve as a result of its inability to open completely (as has been observed by Andresen et al. [35]), and partly due to the fact
that the electron source also causes an overall warming of the apparatus, including the valve. Thus, expansion does not take place from a room temperature source but from one at significantly elevated temperature. Dimer formation with the consequent release of the heat of condensation would also serve to raise the gas temperature but we expect this process, which scales as $\frac{n_s^2}{a}$, to be insignificant because of the relatively low stagnation pressure used.

Similar neutral gas temperatures were obtained when a mixture of 5% $\text{N}_2$ and 95% $\text{He}$ was used. This time the $\text{He}$ metastables were used to obtain the TOF data, as shown in Fig. 3.10. All of this strongly suggests that equilibrium between the translational and rotational degrees of freedom has occurred in our target beam and that this may be specified by a 10 K temperature. Returning to Fig.3.7, we see that some rotational warming must occur during the ionization process since the product ion is roughly characterized by a temperature of 14 K whereas the target neutral is best described by a temperature of $\approx 10$ K. We note that Carrington and Tuckett [18] have observed $N^+_2 B^2 \Sigma_u^+ (v = 0)$ to $X^2 \Sigma_u^+ (v = 0)$ electron beam excited fluorescence in a 5% $\text{N}_2$ in He expansion and obtain a temperature of 23 K for the ion. However, even though they were not able to measure the temperature of the neutral beam, they declare that no rotational warming takes place during the electron-impact process. Our results above show that this is not the case.

We now discuss possible physical mechanisms by which rotational heating takes place during the ionization process. We have discussed earlier some of the secondary
effects which might cause rotational warming. However, in the absence of secondary
effects, we still observe a net transfer of rotational energy to the ion. This may come
about as a result of the rotational population redistribution effected by the electron-
impact process and the associated selection rules for excitation. Muntz [1] developed
a model whereby excitation of the \( N^* \Sigma^+_u \) state occurred via optical (dipole) selection
rules and transition strengths. Such dipole transitions occur with a net angular
momentum change \( \Delta N = 1 \), so it is clear that the rotational population of the excited
B state ion will be smeared out compared to the (assumed) neutral ground state Bol-
tmann distribution. In fact, for such a \( \Sigma_g \) to \( \Sigma_u \) transition (which approximates
the ionization process to the B state), the excited state ion will be described by a
distribution

\[
n_n \approx n_{N+1} S^p_{N+1} + n_{N-1} S^p_{N-1}
\]

(3.10)

where the dipole transition probabilities are

\[
S^p = \frac{N}{2N+1}
\]

(3.11)

\[
S^r = \frac{(N+1)}{2N+1}
\]

(3.12)

In Muntz' work and later refinements, it was rather fortuitous that the electron-
impact-excited \( N_2 X^1 \Sigma_g^+ \) to \( N_2 X^2 \Sigma_u^+ \) transition resembled an "optically allowed"
excitation and could be simplified by ignoring the ejected electron and incorporating
optical transition probabilities. In the present work and in other LIF experiments which
probe the ground state ion, no such simple situation exists. The transition
\( N_2 X^1 \Sigma_g^+ \) to \( N_2 X^2 \Sigma_u^+ \) resembles an optically forbidden transition and in order to
not violate the symmetry selection rule \( \alpha \leftrightarrow s \) (whereby ortho to para interconversion
is forbidden), only even $\Delta N = 2, 0$, are allowed. One might, at first, be tempted to use quadrupole transition strengths in the manner in which Muntz and others have used the dipole line strengths. However, elucidation of the physics of the ionization process might better be achieved by examining the role of the ejected electron. Firstly, it is noteworthy that photoionization and electron spectroscopy measurements (as discussed in the review by Brion and Hamnett [36]) clearly show that formation of the $N_2^+ X^2\Sigma^+_g$ state via dipole excitation occurs with comparable probability to dipole excitation of the $B^2\Sigma^+_u$ state. This implies that the ejected electron must carry away parity and angular momentum such that the overall change in angular momentum is even and satisfies the symmetry selection rule. In fact, the calculations of Duzy and Berry [37] best fit observed photoelectron angular distributions under the assumption of p-wave emission when the ion product is in the ground state. Clearly a p-wave electron can carry away both the angular momentum and parity from the system. This leads us to propose a simple model which explains rotational warming during ionization. We can view the ionization process in terms of an incident electron which induces a transition to an excited complex consisting of positive ion plus ejected electron. The ejected electron may carry away parity and angular momentum as a p-wave such that the overall transition from the neutral $\Sigma_g^+$ to the ionic $\Sigma_g^+$ state satisfies the symmetry selection rule even for an initial dipole excitation to the complex. In this way, the $N_2 X^1\Sigma_g^+$ to $N_2 X^2\Sigma_g^+$ transition might occur by the route illustrated in Fig.3.11. In this figure, the intermediate complex of ion and photoelectron is shown to have a $\Sigma_u^+$ character but could also have been drawn as a $\Pi_u$ state. Carrol and Yoshino [38]
have investigated two optically allowed Rydberg series which converge to the $N_2^+ X^2 \Sigma_g^+$ ion. They come about as a result of the addition of an np electron to the $^2 \Sigma_u^+$ ionic core. They have been designated the Worley-Jenkins series $n\rho \sigma_u \; ^1 \Sigma_u^-$ and the Carrol-Yoshino series $n\rho \Pi_u \; ^1 \Sigma_u^-$. It is simple in concept to extend these series into the continuum where the np electron becomes unbound as a p-wave leading the $^2 \Sigma_u^-$ core. The similarity to autoionization is clear but, presumably, the complex is much shorter-lived. The final rotational state of the $X \; ^2 \Sigma_g^+$ ion would be determined by the triangle relationship among the angular momenta of the excited complex, the ejected p-wave and the $^2 \Sigma_g^+$ core as well as by the symmetry selection rule $\alpha \leftrightarrow s$.

![Diagram](image)

**Figure 3.1**: Model of the ionization process as discussed in the text. Solid arrows indicate electron-impact excitation to the $(N_2^+ + e^-) \; ^3 \Sigma_u$ autoionizing state. Dashed arrows show decay routes from this state to the ground state.
Fig. 3.12 shows the results of a model calculation based on the excitation scheme of Fig. 3.11 where we have assumed dipole line strengths for excitation of the intermediate complex and equal decay probabilities along the indicated paths from the complex to the final ground state ion. Agreement with the data is good and is certainly far better than a calculation based on quadrupole line strengths according the the formula

$$n_N = n_{N-2} S_{N-2}^S + n_N S_N^0 + n_{N-2} S_{N-2}^0$$  \hspace{1cm} (3.13)

where the quadrupole transition probabilities are [39]

$$S_{N-2}^S = \frac{(N + 2)(N + 1)}{(2N + 3)(2N + 1)}$$  \hspace{1cm} (3.14)

$$S_N^0 = \frac{2N(N + 1)}{(2N + 1)(2N + 3)}$$  \hspace{1cm} (3.15)

$$S_{N-2}^0 = \frac{N(N - 1)}{(2N + 1)(2N - 1)}$$  \hspace{1cm} (3.16)

In Fig. 3.12 generated and experimental distributions have been normalized to their peaks. We point out that discrepancies between our model calculation and the data may be due, in part, to our (faulty) assumption of a target ground state Boltzmann distribution. All the evidence so far clearly indicates that the rotational distribution of a molecular gas undergoing supersonic expansion is non Boltzmann. However, deviations from Boltzmann behaviour become important only at higher-\textit{N} levels where the population is already diminished by one or two orders of magnitude. The assumption of a Boltzmann distribution in our model calculation is therefore reasonable.
Figure 3.12 Comparison of generated and experimental rotational level population distributions. The full bar represents an average of the two data sets shown in Figure 3.6. The shaded bar gives the results of a model calculation based on the excitation scheme of Figure 3.11 (see text). The open bar gives the results of a model calculation based on the use of quadrupole rules and line strengths (see text). All distributions have been normalized to their peaks.

We have also not accounted for the effect of cascade which would also lead to a degradation of the rotational population distribution. The work of Stanton and St. John [40] and Rapp and Englander-Golden [41] suggests that the overall contribution of the $A^2\Pi_u$ and $B^2\Sigma_u^-$ states to the total ionization cross section is less than 30% for
energies greater than 100 eV. This indicates that the major portion of the total ionization cross section results from the direct excitation of the ground state ion but that a cascade component may reduce the quality of fit of our model.

As a cautionary note, and in accord with Dagdigian and Doering [42], we again emphasize that the excitations of $N_2^+ X^2 \Sigma_g^+$ and $N_2^+ B^2 \Sigma_u^+$ are inherently different. For this reason, the comparison made by Helvajian et al. [27] of their data to the model calculations of Muntz [1] and Coe et al. [17] is inappropriate since no account has been made of the different selection rules involved in the excitation process.

In Fig.3.13 we show the results of measurements of rotational temperatures covering the impact-energy range 30-300 eV. Above 80 eV the rotational temperature is essentially constant and can be explained in the context of dipole excitation as discussed above. Below 80 eV it is evident that significant warming is occurring which cannot be explained by this model. Fig.3.14 shows a plot of rotational energy [29] versus impact energy. In view of the non-Boltzmann population distribution it is more appropriate to display the data in this way. Also displayed in Fig.3.14 are the data of Nagata et al.[29]. Our rotational energies are about a factor of two smaller than those of Nagata et al. over the whole energy range. Significantly, both data sets show a pronounced increase in rotational energy as the impact energy is lowered below about 80 eV. Our rotational energies are lower than most of those reported in the literature. In the light of the discussion above, we believe that secondary effects may have been more important in some earlier experiments than have been suspected.
Figure 3.13  
Variation of the $^3\Sigma_g^+$ rotational temperature, obtained as discussed in the text, as a function of electron impact energy. Data was taken with a nozzle head pressure of 3 atm and a laser probe delay of 0.5 $\mu$s after the termination of the electron beam.
In the absence of such secondary effects we are still left with the significant increase in rotational energy below 80 eV shown in Fig.3.14. We believe that it is unlikely to be due to interactions between the ejected (scattered) electron and the nascent ion because such interactions would be present at all energies and we find no
reason to invoke any such mechanism at the higher energies. On the other hand, multipole interactions between the incident electron and the target \( \text{N}_2 \) molecule might be expected to become more significant as the incident energy was reduced towards threshold in accord with the observations.

3.4 Conclusions

By monitoring neutral target temperatures with TOF techniques and the ionization product with LIF, we have been able to observe rotational warming which takes place during ionization. We have found that substantial rotational excitation of anionic molecular sample can take place as a result of secondary collisions. In the absence of these effects, significant rotational warming takes place during the ionization process itself. This redistribution of the rotational level population during the formation of the ground state ion has been described in terms of a rudimentary model based on a process analogous to autoionization. This redistribution does not depend on electron impact energy above 80 eV. In the context of our model, this implies that the optical transition probabilities reasonably describe the electron-impact ionization process down to relatively low energy (80 eV). Below this energy it is necessary to invoke the presence of multipole interactions between the incident electron and the \( \text{N}_2 \) molecule, in order to explain the observed effects. We highlight the need for a more complete theoretical description of the ionization process before the LIF technique can be applied to, for example, precise thermometry of gas samples.
3.5 References


SECTION 4

ROTATIONAL RESOLVED LASER INDUCED FLUORESCENCE

STUDIES ON CN X (V = 0, 1) PRODUCED BY ELECTRON-IMPACT

DISSOCIATION OF ACETONITRILE

4.1 Introduction

In basic and applied research absolute cross sections for dissociation of molecules by electron impact are fundamental and important quantities. Excited and ionic state formation cross sections have been measured by a variety of methods, but to date there have been few measurements of the cross sections for the formation of ground state fragments following electron impact. This is because of the difficulty of detecting particles with very low internal or kinetic energies. Before the advent of lasers, detection of dissociation into unexcited neutral fragments seems to have been limited to fast-beam techniques with coincident detection of both fragments and hence complete definition of the dissociation kinematics (P. Cosby et al. [24]), or to techniques based on the adsorption or trapping of the neutral fragments on suitable surfaces. Such techniques have been exploited by Corrigan [1] and particularly by Winters [2] but clearly have limited applicability. So far data have been obtained for the fragmentation of H₂, N₂, CH₄, and C₃H₄ though Winters [2] has indicated that other molecules can also be studied by this technique. The main disadvantage of the technique is that TOTAL dissociation of the molecule is measured and information about the relative importance of the different dissociation channels must be obtained in other ways. The developments of laser induced
fluorescence (LIF) techniques has opened the door to probing electron impact dissociation into specific final states of the product fragments though so far the applicability of the technique seems to have been limited. Schmitt et al. [3] have measured the absolute cross section for the formation of SiH(X) from SiH₃ in a multipole discharge plasma, and Kawazumi and Ogawa [4] have used LIF to measure the absolute cross section for the formation of CN(X) from CH₃CN and BrCN by electron-impact in a pressure cell. The present work seems to be the first crossed-beam measurement.

The cyanide radical (CN) is found extensively in many systems such as interstellar media, comets, atmospheric carbon arcs, low pressure discharge and flames in carbon bearing vapours. The dominant transition observed either in absorption or emission in these systems is the $B^2Σ^+ \leftrightarrow X^2Σ^+$ transition.

Considerable attention has also been devoted to the photochemistry of the cyanide compounds, mostly ICN. These studies have yielded energy distributions for the evaluation of repulsive potential surfaces. Baronavski [5] and Krieger et al. [6] found that the rotational distribution of $CN X^2Σ^+$ after photodissociation from ICN was markedly non Boltzmann, while Fisher et al. [7] found that the rotational distribution was a linear combination of temperature components. Fisher et al. verified that the dissociation channels are strongly dependent on the wavelength of the dissociating laser pulse. At 351 nm dissociation to the $(v=1)$ vibrational level was negligible, whereas at 308 nm it was energetically possible to significantly populate the $(v=2)$ and $(v=1)$ vibrational levels. There has been to
date, no extensive treatment of the dissociation channels for CN produced by electron-impact on any target. In the present study we report on dissociation channels in CH₂CN for electron-impact energies ranging from 30 eV to 300 eV and, using LIF time-of-flight techniques, we measure the translational velocity of the CN radical. The rotational, vibrational and translational energy distributions can help elucidate the dissociation mechanisms.

Electron-impact studies of the CN radical production have been used typically [8] to determine the lifetime of the \( CN B^2 \Sigma^+ \) state. Nagata et al. [9] by observing the polarization of the \( CN B^2 \Sigma^+ \leftrightarrow X^2 \Sigma^+ \) emission after electron-impact dissociation near threshold were able to identify the dominant dissociation process from HCN and DCN. Jackson et al. [10] using a tunable dye laser have measured the radiative lifetimes of the individual rotational lines in a flame. Kawazumi and Ogawa [4] were the first to use laser excitation as a probe of the \( CN X^2 \Sigma^+ \) neutral ground state after electron-impact dissociation. Their experiment took place in a pressure cell using both CH₂CN and BrCN as parent molecules for electron-impact dissociation of CN. They measured the cross sections for the production of both \( CN X^2 \Sigma^+ \) and \( N \frac{\chi}{2} X^2 \Sigma^+ \) electronic ground states, and referenced the CN cross section to the reported values of the absolute ionization cross section of N₂. The measurements performed by Kawazumi and Ogawa [4] however were hampered by the large rotational temperature and associated error for CN in their pressure cell (\( T = 10000 \pm 4000 \) K). The magnitude of their error incurred in their tem-
perature determination made it difficult to quantify the cross section as random fluctuations of about 50% were reported. Kawazumi and Ogawa [4] also performed their measurements for only an electron-impact energy of 200 eV.

In our study, the use of a supersonic beam of CH$_3$CN is an ideal way to transcend the limitations of the static pressure cell. In the supersonic expansion the rotational, vibrational and translational temperature of the CH$_3$CN are expected to be much colder than in a static cell. This yields an unsophisticated rotational system where we can use laser induced fluorescence techniques to probe both the rotational and translational temperature of the CN fragment in addition to measuring the absolute cross-section for its production in specific rovibrational levels of the ground state. In this way we obtain information on the dissociation dynamics as well as on the relative production probabilities.

4.2 Results and Discussion

4.2.1 Experimental Details

A detailed description of the various systems in the experiment have been given above (cf Section 2). A brief remark on those points which pertain specifically to this study should be made however. The supersonic valve used in the nitrogen studies was replaced with a modified Bosch car fuel injector, which had dependable operation above 100°C. The vacuum system used previously was augmented by a LN$_2$ cold trap to provide efficient cryo-pumping of the spectroscopic and ACS grade acetonitrile vapour. Fluorescence photons were wavelength selected by a 10nm bandpass interference filter, centered at 390 nm.
4.2.2 Laser induced rotational spectra

The curve in Fig.4.1 is typical of the type of LIF spectra obtained in the present experiment when observing the B-X \((v'=0,v''=1)\) systems. The data shown in Fig.4.1 were obtained by probing the gas jet about \(2\mu s\) after the termination of a \(6\mu s\) electron beam pulse. There was no significant change in the rotational LIF spectra obtained for delays longer than \(2\mu s\) between the laser probe and the termination of the electron beam, as shown in Fig.4.2. By considering the relative intensities of the B-X (0,0) and B-X (1,1) transitions, the relative cross sections for dissociation to the \(X(v''=0)\) and \(X(v''=1)\) states was determined to be in a 1:0.15 ratio. This was obtained after making suitable allowance for (small) variations with wavelength in detector efficiency and output intensity of the probe beam and taking account of the relevant Franck-Condon factors involved. Attempts were made unsuccessfully to detect the B-X(2,2) R-band at about 385.3 nm but it was too weak. This allowed an upper bound to be placed on the dissociative cross section to the \(X(v''=2)\) state, a ratio of \(X(v''=0)\) to \(X(V''=2)\) production of at most 1:0.05. Vibrational relaxation would cause these relative cross sections measurements to be too low, but little of this is expected because of the long vibrational lifetimes compared to the fluorescence data collecting window (200 ns). Collisional (non-radiative) relaxation is not significant either because we work in the collision free environment of the expansion. Rotational spectra obtained for CN radicals at two points along the axis of the expansion separated by 20 nozzle diameters showed no rotational "warming", which we would expect if there were a significant number
Figure 4.1  LIF rotational spectra obtained for the CN (B-X) band. The laser was introduced 0.002 ms after the termination of the electron beam and an acetonitrile stagnation pressure of 2 atm. The impact-energy was 300 eV.
Figure 4.2

LIF rotational spectra obtained for the CH (B-X) band for two different laser-probe delays after the termination of the electron beam. (a) and (b) represent delays of 0.002 ms and 0.004 ms, respectively.
of collisions occurring. The bandwidth of the dye laser \( (=1 \text{ cm}^{-1}) \) was insufficient to resolve the spin doubling in the \( B^2 \Sigma - X^2 \Sigma \) transition, which amounts to 0.6 cm\(^{-1}\), and hence can be treated as a \( ^1 \Sigma \rightarrow ^1 \Sigma \) transition. To test for the possible effects of polarization of the dye laser beam on the CN rotational distribution, the plane of polarization was rotated 90° with a half-wave plate. The LIF excitation spectra were the same within the precision of replicate scans for the two polarizations, as shown in Fig 4.3.

The LIF signal intensity is directly related to the rotational population in the ground state of the molecule being probed by the laser. More specifically the relationship between the number of molecules \( n_N \) in rotational level \( N \), of the lower state is related to the observed fluorescence intensity \( I_N \), by [12]
Figure 4.3 LIF rotational spectra obtained for the CN (B-X) band for the probe laser at two different polarizations with respect to the plane formed by the detection optics and the electron beam. (a) and (b) represent polarizations "in plane" and "perpendicular" to the plane, respectively.
\[ n_N = C(\Omega) S_N l_N \]  \hspace{1cm} (4.1)

where \( C(\Omega) \) is a term which depends only weakly on the transition frequency, \( \Omega \), and includes the transition moment, the Franck-Condon factor, various geometrical factors and the efficiency of the detection system. \( S_N \) includes the Hoenl-London line strength for the transition and (in case of homonuclear molecules) a nuclear spin degeneracy factor, \( S_N \) depends on whether the upward transition is saturated or not. For the present case of CN the appropriate values of \( S_N \) for the R branch are:

\[ S_N(U) = \left( \frac{1}{2(N+1)} \right) \text{ unsaturated} \]  \hspace{1cm} (4.2)

\[ S_N(S) = \frac{4(N+1)}{(2N+3)} \text{ saturated} \]  \hspace{1cm} (4.3)

Assuming that the rotational population can be described by a Boltzmann distribution at temperature, \( T \), we may write (Herzberg [12])

\[ n_N \propto (2N+1) \exp \left( -\Theta N \frac{(N+1)}{T} \right) \]  \hspace{1cm} (4.4)

where \( \Theta \) is the rotational constant for ground state CN in Kelvin units. Combining
equations (4.1) and (4.4) we see that a plot of \( \log \left( \frac{I_n S_n}{(2N + 1)} \right) \) versus \( N(N + 1) \) should be a straight line from which the temperature can be obtained directly.

In order to establish whether to use Eq.(4.2) or Eq.(4.3) for \( S_n \) we carried out a series of measurement of R-branch rotational spectra in which the dye laser energy was varied. These measurements demonstrated that we were working in the "unsaturated" region and so Eq.(4.2) was applicable. Measurements were also taken to ensure that the LIF intensity varied linearly with driving pressure and electron-beam current.

Boltzmann plots taken at four different CH\(_3\)CN stagnation temperatures are shown in Fig.4.4. Within the error of the measurements the CN rotational temperature was found to be independent of CH\(_3\)CN stagnation temperature (head pressure). A value of \( 83 \pm 5 \)K was obtained at an incident electron energy of 300 eV. Assuming this temperature it is possible to generate a synthetic LIF spectrum and this is shown in Fig.4.5 where it is compared with the actual 300 eV spectrum. The very close relationship between the actual and synthetic spectrum is evident.

Rotational temperature determination using the \( v = 0 \) system depends slightly on the populations of the \( v = 1 \) system because the bands overlap at high \( N \), but since the (1-1) band system of CN at 387.1 nm was very weak, as illustrated in Fig.4.1, there was no difficulty in determining the rotational temperature. It is important to note that the observed rotational temperature did not change for head pressures ranging from one atmosphere (stagnation temperature = 80°) to 5
Figure 4.4 Boltzmann plots representing the CN (X) rotational population distribution as a function of stagnation temperature. Data was obtained by extracting the integrated intensities of the R-branch of spectra similar to those shown in Figure 4.3.
Figure 4.5 Synthetic spectra ($T = 50$ K) calculated for the CN (X-B) rotational LIF spectra and compared to data similar to that shown in Figure 4.1.
atmospheres (stagnation temperature = 130°), as shown in Fig.4.4. This suggests that the actual temperature of the target molecules following the expansion depended only very weakly, if at all, on the initial temperature of the gas before the expansion took place.

Also, shown in Fig.4.6 and Fig.4.7 are rotational spectra and the equivalent Boltzmann plot for the B-X transition of N$_2$*. Here the Boltzmann plot suggests an N$_2$* rotational "temperature" of $23 \pm 3K$ also at an incident electron energy of 300 eV. This is consistent with earlier work [11] from this and other laboratories and may be considered as a typical representative temperature for the parent molecular species in the supersonic expansion. Under this assumption we see that some slight rotational heating may occur in the CH$_3$CN dissociation process. Comparing this rotational temperature with the 10,000K measured by Kawazumi and Ogawa [4] strongly suggests that secondary collisions of some type must have lead to significant rotational warming of the nascent CN in their case.

The rotational temperature of the CN radical was found to depend somewhat on the incident electron energy, as shown in Fig.4.8. The "temperature" increased by about a factor of two as the incident electron energy was raised from 30 eV to 300 eV. This may reflect the fact that different dissociation channels may become dominant as the electron energy is increased. Evidence presented later does in fact suggest that more than one dissociation process is occurring.
Figure 4.6  
Rotational LIF spectra obtained for $\text{H}_2^*$ (X) at 390 nm obtained by electron-impact ionization of $\text{H}_2$ for a stagnation pressure of 3 atm and electron-impact energy of 300 eV.
Figure 4.7 Boltzmann plot of the rotational level populations extracted from data presented in Figure 4.6. The solid line represents a rotational temperature of $23\pm3K$. 
Figure 4.8 Plot of the CN (X) rotational temperature as a function of electron-impact energy. The data is extracted from Boltzmann plots for LIF spectra similar to that shown in Fig. 4.5, where the stagnation pressure was 2 atm and there was a delay of 0.002 ms between the electron beam termination and the probing laser beam.
Because the measured "temperature" of the CN fragment must be close to the actual rotational temperature of the parent molecule it is clear that little torque is being applied to cause enhanced rotation of the CN during the dissociation process. Although the detailed dissociation dynamics depend on the potential energy surfaces of the ground and excited states and the Franck-Condon overlap of the wavefunctions involved, it seems clear from the above evidence that dissociation occurs via a stretching of the C-C bond rather than by any bending vibration perpendicular to this.

4.2.3 Absolute Cross Sections

Following Solomon and Silva [13] and Kawazumi and Ogawa [4] we can elaborate Eq.(4.1) and write the LIF signal intensity from a CN radical in a state N as,

\[
I_{\text{LIF}} = \frac{n_N \sigma_{ab} L P t}{\hbar \omega} Q_{\nu'} \frac{d \Omega}{4 \pi} \eta
\]  

(5)

where P is the laser power, t the laser pulse width, L the path length for electron impact and laser absorption, Q_{\nu'} the branching ratio to the observed transition which is calculated from Franck-Condon factors and transition wavenumbers, \(\sigma_{ab}\) the integrated absorption cross section of the rovibronic transition, \(\frac{d \Omega}{4 \pi}\) the detection solid angle, \(\eta\) the total efficiency of the detection system and \(\hbar \omega\) the photon energy.
of the observed fluorescence. Following formation, the CN radical diffuses out of the interaction region and so we have the following expression for the density $n_N$ of molecules in a particular rotational state $N$,

$$n_N = \frac{\sigma}{k_{out}} \frac{l_o n_o}{f_N}$$

(4.6)

where the CN radical diffuses out of the detection volume with a rate constant $k_{out}$, $\sigma$ is the absolute cross section for its formation, $l_o$ the flux of the incident electron beam, $n_o$ the density of the CH$_3$CN molecules and $f_N$ the distribution fraction of the rotational state $N$. The curve shown in Fig. 4.9 shows the LIF intensity from the CN radical obtained by probing with the laser at different delay times after the electron beam termination with the laser stabilized on a particular rotational line. Analysis of this curve provided a diffusion out rate of $1.11 \times 10^6$ s$^{-1}$ for CN. The distribution fractions were determined making use of Equation (4.4) and the measured rotational temperatures, $T_r$. If the energies, $E_N$ and the statistical weights, $g_N$ of the rotational states probed by the laser are considered we have:

$$f_N = \frac{g_N \theta^{-\epsilon_N/kT_r}}{\sum g_N \theta^{-\epsilon_N/kT_r}}$$

(4.7)
where, in the case of \( \text{N}_2^+ \), care must be taken to include the nuclear statistical factor as well.

The rotational spectra obtained for \( \text{N}_2^+ \) were characterized by a rotational temperature of \( 23 \pm 3 \) \( K \), the temperature derived from the Boltzmann plot in Fig. 4.7. We remark at this point that this temperature is somewhat higher than that recorded in previous studies (cf Section 3). The elevated temperature is understandable considering that the expansion was from a valve heated considerably \( (> 120 \, ^\circ C \) ) above room temperature. This previous work with \( \text{N}_2^+ \) has also shown that the rotational temperature of \( \text{N}_2^+ \) following ionization by electron impact varies with the electron impact energy, especially below 80 eV. The rotational distributions for \( \text{CN} \) and \( \text{N}_2^+ \) were therefore not constant for all impact energies. For an impact energy of 300 eV the distribution fractions \( f_1 (N_2^+) \), \( f_3 (N_2^+) \), and \( f_4 (CN) \) were calculated to be 0.276, 0.189 and 0.152. We can combine equations (4.5) and (4.6) and write the ratio of the absolute cross sections for the production of \( \text{N}_2^+ (X,v=0) \) and \( \text{CN} (X,v=0) \) to get,
Figure 4.9
Plot of the CH (X) LIF intensity as a function of delay between electron beam termination and probing laser beam. The solid line represents an exponential decay with a characteristic "fly-out" rate of $1.11 \times 10^6$ s$^{-1}$. 
\begin{align}
\sigma(CN) &= \frac{Q_{v'v}(N_2^) f_N(N_2^)}{Q_{v'v}(CN)f_N(CN)} \\
X &= \frac{n_o(N_2^) K_{out}(CN) I_{LIF}(CN)}{n_o(CH_3CN) K_{out}(N_2^) I_{LIF}(N_2^)}
\end{align}

(4.8)

Where we have assumed (i) the integrated absorption cross sections ratio is essentially unity, since the oscillator strength for the B-X transitions of CN and N₂⁺ are 0.032 and 0.0348 respectively [14,19], (ii) laser power and electron beam characteristics remain the same for measurements of the LIF fluorescence intensity from the two species, (iii) the sensitivity of the detection system is the same for both species since the fluorescence wavelength of the observed transitions in CN and N₂⁺ are almost the same.

Itikawa et al. [16] have listed cross sections for electron-impact ionization of N₂ and there has been recent work on the total and partial ionization cross sections by Krishnakumar and Srivastava [17] who compare their data with all previous measurements. We assume their cross-sections for N₂⁺ production. In principle we can now estimate the cross sections for N₂⁺ (X) production by subtracting the excited state cross sections from this data. The only states which are significantly excited following electron impact are the A ²Π_u and B ²Σ_u⁺ states. Some measurements have been made of the C ²Σ_u⁺ excitation by van de Runstraat et al.[18]. The state is extensively predissociated for ν ≥ 3. From these measurements it is possible to estimate the total cross section for C-state excitation which is non-dissociative to
be approximately $2 \times 10^{-19}$ cm$^2$ at 100 eV incident electron energy. Since this is less
than 0.1% of total $\text{N}_2^+$ production at this energy, we neglect this contribution and
that of other $\text{N}_2^+$ excited states. $\text{N}_2^+$ (A) state excitation measurements have resulted
in conflicting data sets as discussed by Piper et al.[19]. This is probably due to the
long lifetime of this state, the subsequent difficulty of collecting all the photons
from its optical decay and the need to allow for collisional quenching. The more
recent measurements favour the larger cross-section values. Piper et al. [19] infer
a total cross-section for $\text{N}_2^+$ (A) state production at 100eV of $1.15 \times 10^{-16}$ cm$^2$. The
$\text{N}_2^+$ (b) state cross section has been carefully studied particularly because of the
importance of the 391.4 nm (0,0) band. Taking Borst and Zipf's [20] measurement
of this band at 100 eV of $1.74 \times 10^{-17}$ cm$^2$ together with Stanton and St.John's [21]
extensive relative band intensity measurements leads to a total $\text{N}_2^+$ (B) state cross
section at this energy of $2.8 \times 10^{-17}$ cm$^2$.

Above 100 eV the shape of the measured excitation functions are very similar
and closely resemble the total $\text{N}_2^+$ production cross section. Hence we can estimate
the fractional $\text{N}_2^+$ (X) production at 100 eV and assume that this stays approximately
constant with electron energy. Using the numbers quote above suggests that 31%
(55%,14%) of $\text{N}_2^+$ excitation goes into the X(A,B) states. The 31% predicted for
$\text{N}_2^+$ (X) excitation seems somewhat low. Kawazumi and Ogawa [4] use fractions
of 67%, 25% and 8% for the three states. If we consider photoionization into these
three ionic states, Gallagher et al. [22] have tabulated data indicating that excitation
into the X and A states occurs with comparable probability and that the probability
of B state excitation is about a factor of four lower. It is reasonable to introduce a comparison with photoionization data because the electron-impact excitation functions have shapes which are characterized by optically-allowed transitions from ground state N₂. As a reasonable compromise we assume that the cross sections for X, A and B state excitation are in the ratio of 0.45:0.45:0.10. This rather unsatisfactory situation with respect to the N₂⁺ excitation cross sections leads to an increase in the uncertainty of our measurements.

Since we probe with the laser beam one µs after the end of the electron beam pulse there is more than enough time for the B state to decay to the ground state thus increasing the effective ground state cross section. The A state has a lifetime of at least 10 µs [16] and so only a small fraction of these molecules will have decayed prior to laser interrogation. Finally, we carried out a further LIF measurement to find the fraction of the N₂⁺ (X) molecules which were in the ν" = 1 state. Putting all these factors together allowed us to estimate the effective cross section for formation of N₂⁺ (X, ν = 0) as 9.4×10⁻¹⁷ cm² at 100eV. Since we probe the CN radical also one µs after the end of the electron beam, short lived electronic states of appropriate symmetry can decay radiatively into the ground state. The LIF intensity measurements then represent the cross section for production of CN radicals in the X and B (analogous to the N₂⁺ B state) states. Thus we obtain an increase in the effective ground state cross section as in the case of nitrogen. A future measurement would be to probe the CN radical production nearer to the falling edge of electron beam pulse, before the excited states can decay to the ground
state.

The density of the \( \text{N}_2 \) or \( \text{CH}_3\text{CN} \) at the interaction region (\( X/D = 7.5 \)) can be calculated using [27]

\[
\frac{n}{n_o} = \left( 1 + \frac{\gamma - 1}{2} M^2 \right)^{-\frac{1}{\gamma - 1}}
\]

(4.9)

where \( n_o \), \( n \), \( \gamma \), and \( M \) are the stagnation density, the density at the Mach disk, the ratio of specific heats and the Mach number, respectively. Using the Mach disk measurements of Ashkenas and Sherman [25] and Anderson [26], the ratio of the densities at the interaction region is

\[
\frac{n(\text{N}_2)}{n(\text{CH}_3\text{CN})} = 2.0 \frac{n(\text{N}_2)}{n(\text{CH}_3\text{CN})}
\]

(4.10)

The absolute cross sections for production of \( \text{N}_2^+ \) (\( X, v = 0 \)) from \( \text{N}_2 \) and \( \text{CN} \) (\( X, v = 0 \)) from \( \text{CH}_3\text{CN} \) are shown in Fig. 4.10. A number of points should be noted from this figure. First, the solid line in the figure indicates the shape of the total \( \text{N}_2^+ \) cross-section measured by Krishnakumar and Srivastava [21]. The good agreement between our measured shape and theirs indicates that our electron-beam optics and photon detection optics are behaving satisfactorily. Secondly, we note the shape of the \( \text{CN} \) (\( X, v = 0 \)) production cross section. It rises sharply to a shoulder around 70 eV and then rises more gradually towards higher energies. The peak around 70 eV suggests that new dissociation channels may be contributing to \( \text{CN} \) fragment production. We recall that a similar conclusion was reached earlier
in the discussion regarding the variation of CN rotational "temperature" with impact energy.

From measurements and calculations of the various factors present in Eq. (4.8), we estimate that the cross section for CN \((X,v=0)\) production at 70 eV is \(10.3 \times 10^{-17} \) cm\(^2\) and at 300 eV has risen to \(11.44 \times 10^{-17} \) cm\(^2\). Apart from the error discussed above in the estimation of the effective cross section for \(N_2^*\) \((X,v=0)\) production, other errors of significance were 2% in beam current measurement and approximately 20% in the estimation of relative beam densities. Acetonitrile driving pressures were accurately determined from the temperature of the reservoir containing this liquid and the nitrogen driving pressures were obtained directly from dial gauges. Statistical uncertainties and random fluctuations in laser power contributed a further 10%. Overall the uncertainty in the quoted cross sections is approximately 50%. 
Figure 4.10 Plots of the absolute cross sections for the formation of $N_2^+$ and CN (X) as a function of impact energy. For clarity the CN(X) cross section is shown divided by 2.
4.3 Dissociation Mechanisms

From earlier discussion we have already concluded that CN production occurs via more than one mechanism (i.e. from more than one repulsive surface) and that it probably occurs via linear stretching of the C-C bond. By carrying out LIF measurements downstream of the main electron beam-gas interaction region we were able to probe at least part of the translational energy spectrum of the nascent CN \((X,v=0)\), shown in Fig. 4.11.

Following Zetner et al. [11] we have fitted this data to a velocity distribution of the form [23]
Figure 4.11  LIF-TOF profile of OX (X) for a 1 cm offset between the electron beam and the laser beam. The solid line represents a translational temperature of 130 K as obtained from Equation 3.8.
\[ f(v) \propto v^3 e^{-m(v-v_s)^2/2kT} \]  \hspace{1cm} (4.9)

which describes a Maxwell-Boltzmann distribution characterized by a temperature T superimposed on the stream velocity \( v_s \). \( v_s \) is related to \( v_p \), the peak velocity of the measured distribution by

\[ v_p(v_p - v_s) = \frac{3kT}{m} \]  \hspace{1cm} (4.10)

The best fit corresponds to a translational temperature of 130K. We note that this is somewhat warmer than the translational temperature of \( \text{N}_2^+ \) (\( X, v = 0 \)) of 30K, obtained from the jet expansion of \( \text{N}_2 \) and subsequent electron-impact ionization, where of course no dissociation was taking place. We are thus seeing evidence for the break up of \( \text{CH}_3\text{CN} \) into CN fragments which carry essentially zero kinetic energy away from the dissociation. It is interesting to speculate how this might occur. One, though unlikely possibility is that the \( \text{CH}_3 \) fragment is significantly internally excited and this takes account of any excess energy which might have resulted otherwise. Another possibility is that predissociation occurs into an excited state of CN, possibly the B state, via an appropriate curve crossing. Because of its short lifetime this excited state would have relaxed to the ground state before laser interrogation took place. A further possible explanation is that the initial excitation is to an autoionizing state. The ejected electron carries away the excess energy leaving the molecular ion in an unbound state in which the fragments simply drift
apart. Unfortunately, due to stray direct fluorescence from the electron beam pulse we were unable to probe the very short time region after this pulse with the short path length (1.0 cm) available to us. In an attempt to resolve this short time region an interaction block with a separation of 1.5 cm between electron beam axis and probing laser axis was placed in the experiment and further time-of-flight profiles obtained. The data for these studies is presented in Fig.4.13. These profiles also suggested a best fit translational temperature of 130K, with no further success of resolving the CN velocity distributions for "fast" components. Unfortunately attempts to probe the distributions with larger offsets between the electron and laser beam are hampered by insufficient densities of the CN radical to perform LIF measurements.
Figure 4.12: LIF-TOF profile of CN (X) for a 1.5 cm offset between the electron beam and the laser beam. The solid line represents a translational temperature of 140 K as obtained from Equation 4.10.
4.4 Conclusions

By monitoring CN (X) ground state rotational and vibrational populations with LIF techniques and the translational temperatures of the CN (X) using LIF-TOF measurements, we have been able to elucidate somewhat the dissociation process. We have found that surprisingly little rotational excitation takes place during the dissociation process, the parent molecule’s rotational motion does not transfer to the CN fragment. We have also observed some rotational "heating" of the CN fragment as the impact-energy of the dissociating electron beam is increased. This heating suggests that additional dissociation channels operate at higher electron-impact energy. This conclusion is supported by the shape of the excitation function. By measuring the LIF intensity of the CN radical and comparing this to the LIF intensity of N₂⁺, both produced by electron-impact, we have been able to make original measurements of the absolute cross section for ground state production of CN (X). We emphasize that this is a new technique which can be applied to many dissociation and ionization products in the future, allowing measurements of cross sections unattainable by other means.

4.5 References


[27] J.B. Anderson and J.B. Fenn, Phys. Fluids, 8, 780 (1965)
SECTION 5

LASER INDUCED FLUORESCENCE MEASUREMENTS
ON OH(X, v = 0) PRODUCED BY ELECTRON-IMPACT
DISSOCIATION OF WATER AND METHANOL

5.1 INTRODUCTION

When water atoms are bombarded by electrons a number of lines and band spectra from atoms and molecules are observed. Perhaps the most studied of these is the violet band from the OH A-X transition at 306.4 nm. There has been numerous emission cross section [1-7] and polarization [8,9] measurements which usually attempted to clarify the dissociation process. Emission from OH fragments have been studied in gas discharges [10] and afterglows [11]. Experimenters have used the polarization of the emission following molecular dissociation to study the symmetry of the excited parent states [12]. Applying this to H2O, the negative sign of the near-threshold polarization measured by Becker et al. [8,9] for the OH 0-0 band (except the P1 and P2 lines) suggested that the excited H2O states of symmetry A1 are predominantly involved in the electron-impact dissociation process to $OH(A^2\Sigma^+ \rightarrow H^2S^+ )$. They further suggested that slowly (normal) and quickly (abnormal) moving OH radicals were formed via separate dissociation channels from the same surface. Although at low energy the electron-impact dissociation process does not obey the same selection rules as the photo-dissociation process, at higher electron-impact energies they can be approximately equivalent. Recently the use of lasers to probe the products of molecular dissociation has come to the
forefront of research, and can be applied to OH produced by dissociation. Using this technique Andresen et al. [13] published an exhaustive study of the photo-dissociation of H₂O. Also, OH fragments produced by chemical reaction [14,15] have been probed for radiative lifetime measurements of the OH (A) state and to study vibrational energy transfer. Crosely et al. [16,17] at SRI International have also probed (extensively) OH fragments produced in flames.

The photo-dissociation process is extremely sensitive because the polarization of the dissociation-laser can be rotated to cause dissociation along selected channels in the molecule [13]. The rotational distribution of OH(X) produced by photodissociation has been found to be Boltzmann [18], while non-Boltzmann distributions have been measured for OH(A) produced by photo-dissociation and electron-impact [19]. Andresen et al. [13] also have found that the rotational distributions measured via the Q lines departed significantly from that derived from the P and R lines, something never seen before. They also found that the jet cooled water parent molecule's rotation was transferred to the product OH. They proposed that the resulting behaviour could be explained by examining the dissociation process from the $H₂O^* \ 1B_1$ surface. Andresen et al. [13] have measured the OH(X) rotational temperature produced from jet-cooled H₂O by photodissociation to be 210K (via R and P lines) and 460K (via Q lines). They performed the same measurements on an effusive source of H₂O and found the rotational temperature to be 460K (via R and P lines) and 610K (via Q lines). Kawazumi and Ogawa [20] have measured the rotational temperature of OH (X) produced
from an effusive beam of H₂O by electron-impact (\(~ 100 \text{ eV}\)) as 560K (via R₁ branch) and 470K (via P₁ branch), in relatively good agreement with Andresen et al. [13]. Andresen et al. [13] using the polarization characteristics of both the dissociating and probe radiation were able to study the dissociation process in depth, but did not measure the translational energy of the OH (X). Kawazumi and Ogawa [9] have measured the translational temperature of the fragments by determining the doppler profile of the Q₁(3) rotational line. At electron energies of 100 eV and 30 eV they found the translational temperature to be 420K and 230K respectively. They believed that the OH(X) was produced from the \(^2B_1\), \(^2B_2\) H₂O⁺ and \(^1B_1\) H₂O⁺ surfaces and by deconvoluting the doppler profile into 3 different distributions assigned translational energies to the products from these surfaces. In this experiment we probe the rotational and the translational energies of OH (X) produced from electron-impact dissociation of jet-cooled H₂O at electron energies above 100 eV. In the case of OH from H₂O and also OH from CH₃OH our study should be regarded as a preliminary survey. Detailed quantitative work will be carried out in future studies.

Rotational distributions in \(OH \quad ^2Σ^+ (v = 0)\) have been determined by Mohlmann et al. [21] for electron-impact dissociation of a room temperature H₂O vapour. This was an extension of the work by Beenakker et al. [6] who measured the absolute emission cross section for the OH A-X (0-0) band produced by electron-impact on H₂O. In this investigation we also present data on the production of OH (X,\(v = 0)\) by electron-impact on jet-cooled methanol. By applying the same
techniques described in Section 4 we arrive at a dissociation cross-section.

5.2 The Spectroscopy of \( \Lambda^\Pi \rightarrow X^\Sigma \) Transition

The spectroscopy of OH has been extensively discussed by Dieke and Crosswhite [22] and the following is a brief summary of the notations involved. If we assume the notation of Hund’s case (b) [23], then the spin is not coupled to the internuclear axis, but is instead coupled to the total angular momentum of the molecule (apart from spin), \( N \). The corresponding quantum number for the total angular momentum has the integral values,

\[
N = \Lambda, \quad \Lambda + 1, \quad \Lambda + 2, \ldots \quad (5.1)
\]

The total angular momentum \( J \) is then \( N + 1/2 \) and \( N-1/2 \) for the \( \Pi_\downarrow \) and \( \Pi_\uparrow \) states, respectively. For the \( ^\Pi \leftrightarrow ^\Sigma \) band, shown in Fig.5.1, the selection rules are:

\[
\Delta J = 0, \pm 1 \quad (0 \rightarrow 0) \quad (5.2)
\]

which must be strictly satisfied for optical dipole transitions. For Hund’s case (b) there is also the selection rule \( N \rightarrow N \) and \( N \rightarrow N + 1 \). Therefore transitions which obey both rules form strong branches, while those who violate the \( N \) rule are
Figure 5.1 Schematic diagram of the energy levels of OH, obtained from Moore and Richards [25]. Note that the energy level diagram is not to scale and the levels probed by the P, R and Q lines.
weak (except for small N). These rules allow us to obtain the P, Q and R branches where \( N - 1 \rightarrow N \), \( N \rightarrow N \) and \( N + 1 \rightarrow N \) respectively. We label the branches by indices representing initial and final levels and suppress the second label if both indices are the same, further we see that branches with only one index are those for which both J and N selection rules are satisfied. The "main" branches are those with only one index (strong branches) while the "satellite" branches are those for which only the J selection rule is valid. Care was taken at all times to resolve the main and satellite branches in the distribution measurements.

Parity selection rules yield that P and R lines probe the \( \Pi^\text{+} \) and Q lines probe \( \Pi^\text{−} \) states, which can be seen in Fig. 5.1. The + and - symbols indicate the symmetric and anti-symmetric states (with respect to the rotation axis), respectively.

In this experiment we have constrained the probing laser to the unsaturating regime, where the relative populations in the \( ^2\Pi_i \) \((i = 3/2, 1/2)\) are related to the fluorescence intensity of the \( ^2\Sigma^+ \rightarrow ^X^2\Pi_i \) according to the relation:

\[
 n(J^\prime, v^\prime) \propto \frac{I_{\text{LF}}}{B \cdot P}
\]  

(5.3)

where B is the Einstein transition probability for absorption and P is the laser power. The Einstein transition probabilities are a combination of the Hoenl-London and Franck-Condon factors and have been tabulated for the \( ^2\Sigma^+ \rightarrow ^X^2\Pi_i \) trans-
itation lines by Chidsey and Crosely [26].

5.3 Results and Discussion

5.3.1 The Rotational State Distributions from the Dissociation of Water

Fig 5.2 shows a typical LIF rotational spectra obtained for the dissociation of water by electron-impact at 300eV. Measurements at energies below 300eV were not taken. The wavelength scale used in Fig 5.2 is insufficient to resolve some pairs of rotational lines (e.g., Q and P branches), but care was taken that lines were resolved when possible. Using a Fabry-Perot monitor etalon with a FSR of 1 cm⁻¹, the dye laser fundamental was observed to have no more than 5 modes operating at any one time with 1 mode usually much more dominant than the others. The focussing of the YAG pump beam into the oscillator cavity was usually adjusted so that LIF measurements occurred during the best possible mode structure, typically with only 3 modes visibly operating. The mode competition of the 306.4nm laser radiation was aided since the frequency doubling efficiency varies as the square of the intensity and we expect the weak competing modes to not be a factor in our measurements. It is important to note however that the linewidth of the dye fundamental will be doubled in the frequency doubling process. We expect that the linewidth of the ultra-violet radiation was no more than 0.15 cm⁻¹ during our measurements. Because of the large wavelength range involved in measuring the rotational distributions (> 7nm), and the difficulty in maintaining laser power stability over these wide ranges, continuous scans of the spectra were not usually
Figure 5.2 Rotational LIF spectra obtained for the OH (X-A) band at 307.4 nm. Spectra was obtained for electron-impact dissociation of water at 300 eV and a 0.002 ms delay between the termination of the electron beam and the probing laser. Inset shows the LIF intensity of the P1(1) line.
performed. Instead after cataloging the positions of the lines the laser would be tuned to the transition to be studied, then laser power and mode structure would be adjusted to those used when measuring the other LIF intensities. At worst the ultra-violet intensity fluctuations were no greater than 10%.

It was found that direct fluorescence from the electron-excited OH A-X emission hampered accurate measurements of the LIF intensities from rotationally excited levels with \( N^* > 4 \). In an attempt to minimize this effect an interaction block with a 1.0 cm offset between the electron-beam and laser-beam downstream of the expansion was substituted for the "co-linear" or zero offset block used for the measurements described above. Unfortunately it was found although DC background was substantially reduced, LIF intensities were too low for accurate determinations of the rotational distributions to be made. Work with a 0.5 cm offset block was suspended pending completion of this thesis. Intensities of the Q2, P2, R12 and P12 lines were not measured accurately during this investigation, but it is worth noting though that the intensities of these lines were less than 10% of expected values. This is in disagreement with the trends observed by Andresen et al.[13] who found a slight preference to populate the upper \( ^3\Pi_{1/2} \) state for small angular momentum of the OH radical (J small) and is more similar to that found in the isoelectronic molecule HS where the SH \( ^2\Pi_{3/2} \) has been found to be preferentially populated after photodissociation [30]. As observed by Kawazumi and Ogawa [20] the \( \Pi^+ / \Pi^- \) population ratios were measurably different from those expected from purely statistical arguments. Since \( \Pi^+ \) and \( \Pi^- \) levels are probed by
the P & R and Q lines respectively, this effect was manifested in LIF intensities of the Q lines being larger than expected from theoretical considerations. If we assume the rotational levels probed by the P lines have a rotational "temperature" of \( \approx 200 \) K and remove their contribution to the measured LIF intensity, we are still left with Q intensities larger than that expected, as shown in Table 5.1.

Andresen et al.[13] observed this preferential population of the \( \Pi^- \) levels, an effect especially prevalent at large J. Since we were unable to probe levels where \( N^* > 4 \), we were unable to investigate this process further.

<table>
<thead>
<tr>
<th>N&quot;</th>
<th>Measured ( Q_1 + P_\alpha ) LIF intensity</th>
<th>( Q_1 + P_\alpha ) LIF intensity normalized to ( P_\alpha(1) )</th>
<th>Theoretical ( P_\alpha ) LIF intensity (( T_e = 210)K)</th>
<th>Theoretical Q LIF intensity (( T_e = 210)K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9331</td>
<td>4494</td>
<td>2624</td>
<td>1308</td>
</tr>
<tr>
<td>2</td>
<td>6902</td>
<td>3325</td>
<td>1449</td>
<td>911</td>
</tr>
<tr>
<td>3</td>
<td>5598</td>
<td>2698</td>
<td>656</td>
<td>427</td>
</tr>
<tr>
<td>4</td>
<td>1860</td>
<td>896</td>
<td>220</td>
<td>146</td>
</tr>
<tr>
<td>5</td>
<td>842</td>
<td>406</td>
<td>56</td>
<td>37</td>
</tr>
</tbody>
</table>

Measured \( P_\alpha(1) \) LIF intensity = 4806
Theoretical \( P_\alpha(1) \) LIF intensity = 2315
Normalization factor = 2315/4806 = 0.482

Table 5.1 OH (X-A) LIF intensities extracted from rotational spectra similar to that in Fig. 5.2. Note that the measured LIF intensity of the unresolved \( Q_1 + P_\alpha \) branches (Col.#3) is greater than the expected intensity based on statistical considerations (Col.#4 + Col.#5).
Preferential population of the \( \Pi^- \) levels can be explained using simple pictorial arguments [13]. The electron-excited \( \text{H}_2\text{O} \ \ ^1B_1 \) complex decays as shown in Fig. 5.3. The repulsive forces between the O-H and H-H pairs are shown as open arrows and obviously act in the plane of the \( \text{H}_2\text{O} \) molecule. As a result, after dissociation the OH must rotate in the same plane as the parent \( \text{H}_2\text{O} \) molecular plane. An OH radical is a \( \Pi \) molecule, with an unfilled \( \rho \pi \) lobe perpendicular to the internuclear axis. This lobe has two possible orientations with respect to the plane of OH rotation, either "in plane" (\( \Pi^+ \)) or "perpendicular to the plane" (\( \Pi^- \)). These states are only well defined for high \( J \), at lower \( J \) the states becoming well mixed. These orientations are shown in the upper left of Fig. 5.3. Returning now to the dissociation process, we realize that the \( ^1b_1 \) orbital of the \( \text{H}_2\text{O} \) is similar to the \( \rho \pi \) lobe orientation of the \( \Pi^- \) state. In the absence of any external forces acting on the dissociation process this suggests that there may be preferential population of the \( \Pi^- \) state. As attractive as this simple model is, it remains that the states are only well defined for large OH angular momenta. It is somewhat surprising then that the effect is still measurable for even \( N'' < 4 \). It is for this reason and those mentioned above that more work probing different angular momenta states of OH will be interesting. Following the arguments presented above there should be a measurable difference in LIF intensities for probing radiation of different polarizations. Unfortunately we were in possession of only a \( \frac{\lambda}{2} \) plate made of optical glass (BK7) and were unable to obtain the necessary quartz optics to rotate the polarization of the probing laser radiation. Future investigations will study this area.
Figure 5.3 Schematic diagram of the OH dissociation process in the transition $\text{H}_2\text{O} \left(' \text{B}_1, ' \text{A}_1, \right)$ induced by electron impact. One electron in moved from the filled $1\text{b}_1$ $\text{H}_2\text{O}$ orbital to the $4\text{a}_1$ anti-bonding orbital, leaving one unpaired electron in the $1\text{b}_1$ orbital. The two $\Lambda$ doublet states are shown in the upper left. In the dissociation process shown in the center the $\text{H}$ and $\text{OH}$ decay to the left and right, respectively. We note the unpaired $1\text{b}_1$ orbital's orientation is parallel to that of the pr lobe in the OH.
Fig. 5.4 shows the data from 5.2 reduced to a Boltzmann plot. The rotational temperatures extracted from the R1, R2 and P1 branches are $267 \pm 10 K$, $204 \pm 20 K$ and $200 \pm 20 K$, respectively. This was in good agreement with Andresen et al. [13]. Fig. 5.5 shows the LIF intensities for the Q branch presented in Table 5.1, with the contributions due to the P branch removed, reduced to a Boltzmann plot. The extracted rotational temperature for the Q branch of $223 \pm 50 K$ is not in agreement with that of 475K measured by Andresen et al. [13], but we still left with measured LIF intensities greater than expected from statistical arguments. Ground state levels of high angular momentum (where the $\Pi^-$ state is well defined) should be preferentially populated over states with low angular momentum, leading to higher rotational "temperatures". Future experiments probing ground state levels where N$^>4$ will be a much better test if the electron-impact dissociation process is similar to the photo-dissociation process. There was no systematic investigation of the variations of temperature with electron-impact or stagnation temperature as was performed in acetonitrile studies. Future investigations will probe this area.
Figure 5.4 Boltzman plots showing the rotational temperatures extracted from the data like that in Fig. 5.2. Rotational populations are derived by dividing the LIF intensity by \((2N+1)B\), where \(N\) is the rotational quantum number of the state and \(B\) is the Einstein B coefficient for the transition. Solid lines represent "best-fits" to the data, where the lines have been displaced slightly in order to see the slopes better. The rotational temperatures for the \(R_1\), \(R_2\) and \(P_1\) lines were 267 ±10K, 204 ±10K and 200 ±20K, respectively.
Figure 5.5 Boltzmann plot showing the rotational temperature for the $Q_1$ branch extracted from the data presented in Table 5.1. We have assumed that the $P_2$ branch has a rotational temperature of 210K and have removed its contribution to the LIF intensity since the $Q$ and $P$ branches were unresolved in the experiment.
An LIF-TOF profile of the OH (X) Qv(2) line is shown in Fig. 5.6. This was obtained using a 1.0 cm offset between the electron and laser beams and measuring LIF intensities as a function of time after the electron beam pulse at an impact energy of 300 eV. The solid line in Fig. 5.6 represents a "best-fit" theoretical distribution obtained using eq (3.8) (where T = 200 and n = 3), indicating a translational energy of approx. 26 meV. There have been no other translational temperature measurements of OH(X) following electron-impact dissociation in a jet to date. Kawazumi and Ogawa [20] have measured the doppler profiles of the Q1(3) lines following electron-impact dissociation with 150 eV electrons in a H2O effusive source and determined a predominant translational temperature of 420 K and two other components which they identify as dissociation from other H2O surfaces and thermal motion. At present because of the quality of the fit, we see no reason to de-convolute the TOF spectra into arbitrary separate components. The translational energies of H+ (n = 3, 4) produced by electron-impact on H2O have also been determined by Kurakawi et al. [27] using doppler profile measurements. Any doppler profile measurements in this experiment were hampered by the insufficient bandwith of the laser and the fact that there was substantial doppler broadening due to the stream velocity of the gas jet.

Utilizing conservation of momentum considerations in the dissociation process the translational energy of the H should be seventeen times larger than that of the OH fragment, ie 0.434 eV. The schematic energy diagram of H2O is shown
Figure 5.6 LIF-TOF profile of OH after electron-impact dissociation from water. The solid line represents a translational temperature of 200 K as obtained from Equation 4.9 with an offset of 1 cm between the electron and laser beams.
in Fig. 5.7 [20], where the surfaces from which OH(X) may be formed having been identified as the \( H_2O^* \tilde{B}(^2B_2) \), \( H_2O^* (^2B_1) \) and \( H_2O (\tilde{A}^1B_1) \) [31-34]. From measurements done by Andresen et al.[13], OH(X) has been found to be produced exclusively in photo-dissociation of water via the process

\[
H_2O (^1A_1) \rightarrow H_2O (\tilde{A}^1B_1) \rightarrow OH (X) + H \quad (n = 1) \tag{5.11}
\]

with the energy partitioning for the products to be

\[
f_T:f_V:f_R = 0.885:0.095:0.02 \tag{5.12}
\]

Kawazumi and Ogawa [20] also identified this as the predominant process in the electron-impact dissociation of water in an effusive beam. Utilizing this partitioning scheme the translational energies of the OH(X) and H \((n=1)\) produced according to eqn. (5.11) should be in the range of 0.073-0.171 eV and 1.25-2.91 eV, respectively, which does not agree with our measured translational energy for OH(X). Calculated OH(X) translational energies from the \( H_2O^* (\tilde{B}^2B_2) \) and \( H_2O^* (^2B_1) \) surfaces are expected to be \( \approx 0 \) and 0.23-0.41 eV, respectively. Our results suggest that OH(X) may possibly be formed via the process

\[
H_2O (^1A_1) \rightarrow H_2O^* (\tilde{B}^2B_2) \rightarrow OH (X) + H^* \tag{5.13}
\]
Figure 5.7  Schematic diagram of the potential energy surfaces of H_2O and H_2O with the dissociation limit.
5.3.2 The Rotational State Distributions from the Dissociation of Methanol

The rotational LIF spectra typically obtained for electron-impact dissociation of methanol is shown in Fig. 5.8. This data was obtained for an electron-impact energy of 300 eV and a delay of 2 μs between the termination of the electron-beam and the probing laser beam. Rotational temperatures were extracted from the Boltzmann plots presented in Fig. 5.7. For the R₁, R₂ and P₁ branches the rotational temperatures were all found to be $360 \pm 30 \, K$, within the statistical error bars on the measurements. These are the first measurements of the rotational temperatures of OH(X) following electron-impact dissociation of CH₃OH. The temperatures are some 50% larger than those obtained for dissociation from water, but this is to be expected if we observe the structure of the methanol molecule (Fig. 5.4b). If dissociation was to occur along the C-O bond, the resultant torque applied to the OH radical would cause rotational excitation. A rotational temperature for the Q₁ branch can be extracted by using the same procedure applied to the Q₁ branch LIF intensities after dissociation from water. If we assume a rotational temperature of 360K for the P₁ branch and subtract its contribution to the LIF intensities of the unresolved Q₁ + P₁ branches, the rotational temperature of the Q₁ branch is $380 \pm 80 \, K$. 
Figure 5.6 Rotational IIF spectra obtained for the OH (X-A) band at 306.4 nm. Spectra was obtained for electron-impact dissociation of methanol at 300eV and a 0.002 ms delay between the termination of the electron beam and the probing laser.
Figure 5.7 Boltzman plots showing the rotational temperature extracted from the data like that in Fig.5.6. Rotational populations are derived by dividing the LIF intensity by \((2N+1)B\), where \(N\) is the rotational quantum number of the state and \(B\) is the Einstein \(B\) coefficient for the transition. Solid lines represent "best-fits" to the data. The rotational temperatures for the \(R_1\), \(R_2\) and \(P_1\) lines were 360±30K, 370±30K and 350±20K, respectively.
Figure 5.9: Schematic diagram of the methanol molecule. If the dissociation process does not proceed through a line joining the methanol center mass and the OH center of mass, then there will be a resultant torque applied to the OH radical.
5.3.3 Cross Section Measurements for OH (X)

The curve in Fig.5.10 represents the emission cross sections measured for the electron-impact dissociation of water as a function of electron-impact energy. Also shown in Fig 5.10 are the emission cross sections obtained by Beenakker et al.[6]. It is clear from the data that the emission cross section closely follows the shape of the cross section measured by Beenakker et al.[6], where the quickly rising cross section at low energy is characteristic of an optically-forbidden excitation process [28,29]. In an optically-allowed excitation the cross section peaks more slowly and falls off slowly towards higher energies. An electron exchange process however has a cross section which decreases rapidly after reaching the maximum. Since the fall of the cross section is slower from those expected for a pure spin exchange process the observed cross section is probably the superposition of excitation to singlet and triplet states. The cross section at high energy must reflect only the contributions of optically allowed transitions to a singlet state.

The curve shown in Fig. 5.11 represents the emission cross section for OH (A-X) obtained for electron-impact dissociation of methanol as a function of electron impact energy
Figure 5.10 OH (A-X) emission cross section as a function of electron-impact energy for the dissociation of water. The solid curve represents the investigations of Beenakker et al. or Tsurubuchi et al., whereas the solid circles represents this study.
This investigation
\[ \text{CH}_3\text{OH} + e \rightarrow \text{OH}(A \ X) \]

\[ X \text{**} = 10 \]

 Beenakker et al.
\[ \text{H}_2\text{O} + e \rightarrow \text{OH}(A \ X) \]

Figure 5.11 Energy dependence of the OH(A-X) emission cross sections for the electron impact dissociation of methanol (top curve) and water (bottom curve; Beenakker et al. [6]). For comparison purposes the cross section for the production of OH(A) via the dissociation of methanol is shown multiplied by 10.
The data were obtained by monitoring broadband emission from the 306.4 nm system using an interference filter centered at 306.3 nm with a 10 nm bandpass. The interference filter was linear over the region of fluorescence and we do not expect it to distort the cross sections. The solid curve is the emission cross section from OH (A-X) for electron-impact dissociation of water. It was against this cross section that an absolute emission cross section for dissociation from methanol was calculated. Care was taken during the measurements to have the same electron beam and stagnation pressure characteristics for both methanol and water. When it was not possible to reproduce electron beam characteristics the data for water and methanol were separately normalized to their electron-beam currents. In all cases the data was normalized to calculated densities of methanol and water at the interaction region using

\[ \frac{n}{n_o} = \left( 1 + \frac{\gamma - 1}{2} M^2 \right)^{-\frac{1}{\gamma - 1}} \]  (5.4)

where \( n, n_o, \gamma \) and \( M \) are the density at the Mach disk, the stagnation density, the ratio of specific heats and the Mach number, respectively. As is clear from Fig. 5.11, we found that OH(A) production from methanol was down by a factor of 9 over OH(A) production from water.

We also carried out LIF measurements for production of ground state OH(X) fragments from water and methanol. Fig. 5.12 represents the relative cross sections for the production of OH (X) following the electron-impact dissociation of water.
Figure 5.12. Relative cross sections for the formation of ground state OH(X) as a function of energy for the electron impact dissociation of water (top curve) and methanol (bottom curve). The solid line represents a "best fit" through the data representing the cross section for the formation of OH(X) via the electron impact dissociation of water.
and methanol as a function of electron impact energy. The solid curve is a line of "best-fit" drawn through the cross section for the formation of OH (X) from water to achieve a smooth curve. The data was obtained for a delay of 2 µs between the termination of the electron beam and the probing laser beam and a stagnation pressure of 2 atm. In both cases the laser was stabilized on the Q<sup>3</sup>(3) line. Data was normalized to relative densities at the Mach disk using eqn. (5.4). The data in Fig. 5.12 is normalized for the different rotational distributions using fractional populations for a Boltzmann distribution as described in Eq. (4.7). Although the rotational temperatures extracted for the Q branches are indeterminate [cf 5.3.1], we choose the temperatures of the P and R branches as a reasonable compromise. Because of fluctuations in the laser power (<10%), electron beam current (<2%) , the uncertainty in rotational fractions (<10%) and the statistical errors for the measured LIF intensities we assign an error of 50% to the measured cross sections. The cross section for the formation of OH from water is similar in shape to that measured for the emission cross section in Fig. 5.8, characterized by a gradual decrease in ground state atoms formed as the impact energy increases.

It is possible that most of the OH molecules may be formed initially in excited states which cascade rapidly to the ground X state. If this was the case then the similarity between the emission and LIF data would be trivially understood. Some evidence supporting this argument is the low observed translational temperature (Section 5.3.1). Following the same arguments as used in the case of CN production one might propose initial excitation to a state which was then predissociated by a
curve crossing to a surface leading to OH(A). This would radiatively decay to OH(X) before interrogation by the laser. Further measurements need to be performed to confirm this hypothesis. In the case of methanol the decrease in the cross section is not as rapid as in water, but is typical of the optically allowed cross sections. Future work will also put the relative cross sections shown in Fig. 5.12 on an absolute basis using a modification of the normalization techniques discussed for the CN measurements.

5.4 Conclusions

We have measured the rotational distributions of OH (X) following the electron-impact dissociation of water and methanol. In the case of water we have shown that the II⁻ is preferentially populated even for low J, where the II⁻ and II⁺ states are not well defined. The rotational temperature of the states probed by the R and P lines has been determined to be approximately 200 K, in good agreement with Andresen et al.[13] We have measured for the first time a TOF profile for the OH (X) following dissociation from water, the distribution characterized by a translational temperature of 200K. This translational temperature suggests different processes may occur in electron-impact dissociation in a supersonic expansion than that suggested by doppler profile measurements done on electron-impact dissociation in an effusive beam[20].

We have also measured for the first time the emission cross section for the OH (A-X) transition and cross section for the formation of ground state OH (X) following electron-impact dissociation of methanol. The absolute emission cross
section for methanol was obtained by referencing the measurements against the known absolute emission cross section for the OH (A-X) transition following electron impact dissociation of water. For the first time we have also measured the shape of the cross sections for the formation of OH(X) as a function of impact-energy following dissociation from water and methanol. We emphasize the usefulness of the techniques presented above and the need for future work in measuring the total cross section for the formation of OH in all its states following electron-impact on water.

5.5 References


Transfer, 2, 97 (1962).


OVERALL SUMMARY AND SUGGESTIONS FOR FUTURE WORK

The apparatus has demonstrated a convincing ability to resolve interesting processes which occur during electron-impact ionization and dissociation. In Section 3, we have shown that the tunable dye laser can probe the distribution of the rotational levels and the translational energy of N$_2^+$ after electron-impact ionization. We also presented a simple model to explain observed features by including an intermediate complex of ion and photoelectron in the electron-impact ionization process. This model yielded results superior to other models such as simple dipole or quadrupole interactions.

There are several directions in which the work with electron-impact ionization of molecules can be pursued, which are within the capabilities of the apparatus. The electron-impact ionization process can be studied in various other molecules. The rotational heating of the ion can be studied as the supersonic expansion proceeds by probing with the laser at various distances downstream of the expansion. The rotational distributions can also be probed inside the time-of-flight envelope of the ion, elucidating any relationships which may exist between translational and rotational energies. Perhaps the most interesting area would be with an improved low-energy (<15eV) electron source. At present there has been no work done on probing the products of electron-molecule collisions at threshold energies. We
expect this to be a rich field of study in electron-impact dissociation studies especially. A magnetically focussed electron source capable of $>100\ \mu A$ at 10 eV is being evaluated at present.

There is still much work left to be done in the area of electron-impact dissociation. There are very few other groups studying this phenomenon and a plethora of available parent molecules which can be studied. The rotational and vibrational distributions of the CN fragment were investigated in Section 4 after electron-impact dissociation from acetonitrile. We found little rotational, vibrational or translational excitation of the CN fragment subsequent to dissociation and speculated on the mechanisms responsible. By probing the rovibronic populations and translational energy of the CH fragment (which must be present) a clearer picture of the dissociation process may be formed. Absolute cross sections for the formation of ground state CN were measured by comparisons between the LIF intensities from ground state N$_2^+$ and CN after electron impact on N$_2$ and CH$_3$CN, respectively. The absolute cross section measurements for the production of ground state radicals can be improved substantially by probing closer to the dissociating electron-beam pulse, before excited states can decay to the ground state.

In Section 5 we presented preliminary results obtained for the electron-impact dissociation of OH from water and methanol. By probing the rotational distributions of the OH we were able report on the preferential population of certain states. These results compared favorably to those obtained by other studies. There are still many areas which can be studied however. The variation of rovibronic
populations with electron-beam energy and laser polarization are especially very interesting. With the new low-energy electron beam source, the dissociation process at threshold can be probed. With better measurements of the rotational distributions (especially at J>4) comparisons between the dissociation processes in water and methanol can be made with greater accuracy.

In the future we can also envision the possibility of probing metastable atomic states with a low-energy electron-beam. There has been little work in this field due to the very low fluorescence levels expected, the major problem being low densities of excited states. With the combination of the supersonic expansion and high energy laser significant populations of metastable states may be achieved if we excite with the laser to the metastable level via a two-photon process or a single-photon process to some higher state which decays radiatively to the metastable state. This is a very interesting area of study because measurements of cross-sections from excited states are very few and much in demand by pure and applied researchers.
CURRICULUM VITAE

PUBLICATIONS:

Laser induced fluorescence measurements of OH(X) produced by electron impact dissociation of H₂O and CH₃OH. M. Darrach and J.W. McConkey. Chem. Phys. Lett. (pending)

Laser induced fluorescence measurements of the B \( ^2Σ^+ \) state of CN produced by electron impact on CH₃CN.
M. Darrach and J.W. McConkey
J. Chem. Phys. (pending)

M. Darrach and J.W. McConkey

Rotationally resolved electron impact ionization of N₂ in a supersonic jet.
P.W. Zetner, M. Darrach, P. Hammond, W.B. Westerveld, and J.W. McConkey

Quenching of 6s6d and 6s7d Hg atoms by Hg⁻-Hg, Hg-Ar and Hg-N₂ collisions.
M. Darrach, R.J. Niefer, J.B. Atkinson and L. Krause
Fine-structure mixing of 6s6d states by collisions with ground state Hg, Ar atoms and N₂ molecules.
R.J. Niefer, M. Darrach, J.B. Atkinson and L. Krause

CONFERENCE SUBMISSIONS:


Rotationally resolved electron impact ionization of N₂ in a supersonic jet. Gaseous Electronics Conference. Atlanta, USA (1987)

Fine structure mixing cross sections for 6s6d Hg atom and noble gas collisions. Canadian Association of Physicists Meeting, Edmonton, Canada. (1986)

Collisional and radiative processes involving excited Hg atoms. Division of Atomic and Molecular Physics, Toronto, Canada. (1985).
VITAE AUCTORIS

I was born in Halifax, Nova Scotia, Canada on June 30, 1962. I enrolled in the University of Windsor in September 1980 and in April 1984 I graduated with my Honours Bachelor of Science (Physics). I was on the President's Roll of Scholars during my third and fourth undergraduate years. Further, I received the Nicholas Copernicus Award in Physics (1983 and 1984) and the National Science and Engineering Research Council Summer Undergraduate Award during the summer of 1984. I continued at the University of Windsor for the next two years pursuing my Master of Science, which I received in May 1986. During this time I was under the guidance of Dr. L. Krause and was awarded the National Science and Engineering Research Council Post-Graduate Award for the years of 1985 and 1986. Following graduation I moved to Dr. J.W. McConkey's group in September 1986. I was again awarded a NSERC Post-Graduate Award and under Dr. McConkey's supervision this research was carried out.