

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor MI 48106-1346 USA
313/761-4700 800/521-0600

**Experimental Studies of the Electron-Impact Induced
Dissociation and Dissociative Excitation of Simple Halogen
Containing Molecules**

by
Ralph B. Siegel

A dissertation submitted to the Graduate Faculty in Physics
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy, The City University of New York

1996

UMI Number: 9618104

**Copyright 1996 by
Siegel, Ralph B.**

All rights reserved.

**UMI Microform 9618104
Copyright 1996, by UMI Company. All rights reserved.**

**This microform edition is protected against unauthorized
copying under Title 17, United States Code.**

UMI
**300 North Zeeb Road
Ann Arbor, MI 48103**

© 1996

Ralph B. Siegel

All Rights Reserved

This manuscript has been read and accepted by the Graduate Faculty in Physics in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

1/29/96
Date

[Signature]
Chair of Examining Committee

1/29/96
Date

Joseph B. Trivelpiece
Executive Officer

Harold Mittleman

Martin L. S. G. are

[Signature]
Supervisory Committee

THE CITY UNIVERSITY OF NEW YORK

Abstract

Experimental Studies of the Electron-Impact Induced Dissociation and Dissociative Excitation of Simple Halogen Containing Molecules

by

Ralph Siegel

Adviser: Professor Kurt Becker

Electron-impact induced dissociative excitation of SF₆, CF₄, NF₃, CCl₂F₂, and BCl₃ was studied by identifying the strongest emission features following electron-impact and measuring the absolute photoemission cross sections for these emission features. Atomic fluorine (FI) resonance radiation centered at 97.5 and 95.5 nm were the most intense emission features for the fluorine containing molecules. In most cases, unique identification of the dissociation channel leading to the production of the emitting fragment was possible. Total fragmentation was dominant in SF₆, CF₄, and NF₃. Partial fragmentation was more prominent in CCl₂F₂, and BCl₃. A new "triple-beam" experiment designed to study electron-impact induced dissociation was built in which absolute electron-impact induced dissociation cross sections are measured by using laser induced fluorescence (LIF) to measure the absolute number densities of dissociation products left in the ground state. We use an effusive gas beam and a continuous electron beam in conjunction with a pulsed tunable dye laser and gated detection. The use of saturated LIF is emphasized. Preliminary data for the $N_2 + e^- \rightarrow N_2^+(X^2\Sigma_g^+) + 2e^-$ reaction was obtained. Suggestions for overcoming technical challenges and future areas of research are made.

Dedication

This work is dedicated to my loving wife Susan and my two year old son Jacob, without whose support and encouragement this work would not have been possible.

Acknowledgments

I owe a great debt of gratitude to my advisor, Prof. Kurt H. Becker, who taught me how to be an experimental physicist with a minimum of interference which required an extraordinary amount of patience and wisdom. I would also like to thank Mr. Jonathan Friedman, Dr. Michael Cavicchia, and Mr. Peter Kurunzi for lively discussions and useful suggestions, and especially Dr. Vladimir Tarnovsky for his insightful criticisms. In addition, thanks must go to Mr. Jerry Altzman for helping me modify the software accompanying the SR400 photon counter, and Mr. Eric Splaver for writing custom routines for use with the SIMION computer program. Lastly, I would like to thank Mr. Joe Altman, the foreman of the machine shop in the science center at City College for invariably improving designs submitted to him, and the machinists, Linden and Joseph for invariably finishing my jobs ahead of schedule.

Table of Contents

I. Introduction	1
Part I. The Photoemission Experiment	
II. Background	4
Excitation, dissociative excitation and photoemission cross sections	4
Differences between atoms and molecules	6
Kinematics	7
Properties of the emitted radiation	8
Relation to laboratory measurements	12
III. Experimental Considerations	14
Overview of the Method	14
Apparatus and Procedure	14
The Interaction region	18
Electron beam energy spread	18
Detection sensitivity of the photon detection system	19
Signal incident on the monochromator	20
Signal obtained from the photon detector	21
Normalization and calibration	23
Wavelength sensitivity of our photon detector systems	24
Normalization to gas pressure	27
Electron Beam Energy Calibration	29
IV. Results and Discussion	31
Fluorine 3p→ 3s emissions from SF ₆ , CF ₄ , NF ₃ and CCl ₂ F ₂	32
Fluorine 3s(² P)→ 2p emissions from SF ₆ , CF ₄ , NF ₃ and CCl ₂ F ₂	36
Fluorine 3s(⁴ P)→ 2p emissions from SF ₆ , CF ₄ , NF ₃ and CCl ₂ F ₂	42
Ultraviolet emissions (200-300 nm) from BCl ₃	45
Optical emissions (2000 -6000 Å) from NF ₃ , CF ₄ , and SF ₆	49

Part II. The Triple Beam Experiment

V. Introduction	55
VI. Operating Principles and Theoretical Background	58
Rotational Structure of the $N_2^+(B^2\Sigma_u^+ \leftrightarrow X^2\Sigma_g^+)$ Band System	58
The Electronic Structure and Ionization Mechanisms of N_2	63
Estimate of the $N_2(X^1\Sigma_g^+) + e^- \rightarrow N_2^+(X^2\Sigma_g^+) + 2e^-$ ionization cross section	65
Laser Induced Fluorescence	69
Basic Formulation and its Limitations	70
Polarization and Anisotropy in the Unsaturated Regime	74
Saturated Regime	75
VII. Design and Operation of the Apparatus	79
The Vacuum and Gas Delivery Systems	80
The Laser System	81
The Excimer Laser	82
The Dye Laser	83
Laser Pulse Characteristics	87
The Electron Beam	93
Computer simulation of the electron beam focal properties	96
The Photon Detection System	101
The Gas Beam	107
VIII. Optogalvanic Calibration and Linewidth Measurement	111
Introduction	111
The tuning mechanism of the dye laser	115
The Optogalvanic Line Shape and Laser Linewidth	117
IX. Experimental Methods and Procedures	123
$N_2 + e^- \rightarrow N_2^+(B^2\Sigma_u^+) + 2e^-$	124
$N_2 + e^- \rightarrow N_2^+(X^2\Sigma_g^+) + 2e^-$	129
– Techniques for the effective use of the laser system	130
The SR400 Gated Photon Counter	132
Photomultiplier tube blinding	133
Scattered laser light	135
Tuning the dye laser	138

Laser power required for saturation	141
Estimated LIF Signal	146
X. Results and Discussion	152
Results	152
Discussion	154
XI. Conclusions and Suggestions for Further Research	157
The Photoemission Experiment	157
The "Triple-Beam" experiment	158
Bibliography	163

List of Figures

Figure (2.1)	7
Figure (2.2)	10
Figure (2.3)	11
Figure (3.1)	15
Figure (3.2)	16
Figure (3.3)	18
Figure (3.4)	25
Figure (3.5)	25
Figure (3.6)	26
Figure (3.7)	27
Figure (4.1)	32
Figure (4.2)	33
Figure (4.3)	34
Figure (4.4)	36
Figure (4.5)	37
Figure (4.6)	38
Figure (4.7)	38
Figure (4.8)	40
Figure (4.9)	44
Figure (4.10)	45
Figure (4.11)	46
Figure (4.12)	48
Figure (4.13)	49
Figure (4.14)	52
Figure (6.1)	59
Figure (6.2)	62
Figure (6.3)	67
Figure (6.4)	75
Figure (7.1)	79
Figure (7.2)	80

Figure (7.3)	84
Figure (7.4)	85
Figure (7.5)	88
Figure (7.6)	89
Figure (7.7)	89
Figure (7.8)	90
Figure (7.9)	93
Figure (7.10)	94
Figure (7.11)	98
Figure (7.12)	99
Figure (7.13)	100
Figure (7.14)	100
Figure (7.15)	103
Figure (7.16)	104
Figure (7.17)	105
Figure (7.18)	106
Figure (7.19)	108
Figure (7.20)	109
Figure (8.1)	112
Figure (8.2)	112
Figure (8.3)	113
Figure (8.4)	115
Figure (8.5)	119
Figure (8.6)	120
Figure (9.1)	126
Figure (9.2)	127
Figure (9.3)	133
Figure (9.4)	135
Figure (9.5)	136
Figure (9.6)	137
Figure (9.7)	139
Figure (9.8)	141
Figure (9.9)	143

Figure (9.10)		145
Figure (10.1)		152
Figure (10.2)		153
Figure (10.3)		154

List of Tables

Table (3.1)		24
Table (4.1)		35
Table (4.2)		36
Table (4.3)		39
Table (4.4)		42
Table (4.5)		43
Table (4.6)		47
Table (6.1)		74
Table (7.1)		83
Table (7.2)		107
Table (8.1)		114
Table (8.2)		118
Table (8.3)		118
Table (9.1)		128
Table (9.2)		147

I. Introduction

Dissociative processes of molecules are important from two points of view. First, from the point of view of fundamental physics, they allow direct investigation of the quantum states involved in the dissociative process. Specifically, by monitoring the emission following dissociative excitation, new excited states of the parent molecule or of a product species may be discovered. Also, from the nature of the emission (discrete lines, bands, or continuum), the kind of species (atom, molecule, or radical), and the kind of state(s), bound or repulsive, responsible for the emission may be deduced. Also, using time-of-flight (TOF) techniques to measure the kinetic energy distribution of dissociation products, the shape of potential energy surfaces can be deduced. Second, from an applied point of view, because they are a "copious source of photons, kinetically energetic atoms and ions, chemically active metastable species, and short-lived excited states", dissociative processes are "important in many industrial applications which use gaseous discharges" (Zipf, 1984). Also, because they are a copious source of radiation, dissociative processes are important in practical problems such as the degradation of the ozone layer and the interpretation of airglow data in the atmosphere.

Electron-impact induced dissociative processes, and in particular, electron-impact induced dissociative processes involving halogen-containing molecules are particularly relevant today because of their importance to the developing technology of low-temperature processing plasmas. Applications such as the etching of microelectronic circuits, the deposition of high quality thin films, and plasma-assisted surface modifications are the direct result of the developments in this technology. Typically, the species responsible for the surface reactions inside a low temperature processing plasma is a halogen atom or ion, or a halogen containing molecular radical produced through an

inelastic collision between an electron and a molecule of the feedstock gas of the plasma. For precise control of the characteristics of the material processed by the plasma, knowledge of the equilibrium number density of the various reactive species inside the plasma is essential. Therefore, there is a critical need for cross sections for electron-impact induced processes relevant to the creation and destruction of these species (Becker, 1994).

The present work is divided into two parts. The first part concerns the electron-impact induced dissociative excitation of the simple halogen containing molecules SF_6 , CF_4 , NF_3 , CCl_2F_2 , and BCl_3 , which are commonly used low temperature processing plasma feedstock molecules. Electron-impact induced dissociative excitation of these molecules was investigated by measuring the absolute photoemission cross sections for various electron-impact produced emission features, ranging in wavelength from the visible to the VUV. The photoemission cross sections were measured using the optical method in a crossed beam geometry under single collision conditions. The relevant experimental aspects of the optical method are discussed, with particular emphasis on the normalization procedures used to convert the relative cross sections into absolute cross sections. In addition, the relationship between dissociative excitation cross sections and photoemission cross sections, vis-a-vis cascade and branching ratios is discussed.

The second part describes an experiment designed to measure absolute electron-impact induced dissociation cross sections using laser induced fluorescence (LIF). The application of LIF to the measurement of ground state populations produced by electron-impact under single collision conditions has been tried before. Using a supersonic gas beam and a pulsed electron beam, (Darrach, 1990) measured the cross section for the electron-impact induced dissociation of N_2 ; *i.e.*, $\text{N}_2 + \text{e}^- \rightarrow \text{N}_2^+(\text{X}^2\Sigma_g^+) + 2\text{e}^-$, with an uncertainty of 50%.

We have used an effusive gas beam and a continuous electron beam in an effort to measure the cross section for the same reaction. The use of an effusive gas beam and a continuous electron beam enables a data reduction procedure less prone to systematic errors. However, the fluorescence produced by the LIF process is identical with a portion of the fluorescence produced in the reaction $N_2 + e^- \rightarrow N_2^+(B^2\Sigma_u^+) + 2e^-$ and, because the electron beam is continuous, both fluorescence signals are produced simultaneously. Therefore, the LIF signal is harder to detect. As far as is known, we report the first attempt to detect an LIF signal under these conditions (*i.e.*, continuous electron impact source using an effusive gas beam with single collision conditions, and LIF signal detected simultaneously with the electron-impact produced fluorescence from the excited state).

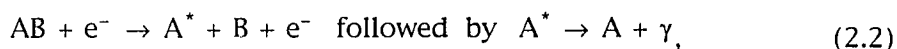
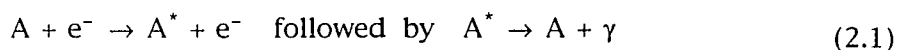
Since a new experimental apparatus was built for this experiment, the design of each component part is discussed in detail, with particular emphasis paid to the laser system. The optical properties and electronic structure of the $X^2\Sigma_g^+$ ground state and $B^2\Sigma_u^+$ excited state of N_2^+ relevant to detecting the LIF signal are given. An estimate of the $N_2 + e^- \rightarrow N_2^+(X^2\Sigma_g^+) + 2e^-$ cross section using available experimental data and the Bethe-Born approximation is made. The theory of laser induced fluorescence is given using both integrated and directional Einstein coefficients, the differences between unsaturated and saturated LIF are pointed out, and the benefits of using saturated LIF are emphasized. The experimental method is developed, again with particular emphasis on the use of the laser system. Using the laser output, the lifetime of the $B^2\Sigma_u^+$ excited state of N_2^+ was measured and agreement with previous results was obtained. In addition, a preliminary rotationally resolved excitation spectrum of the $X^2\Sigma_g^+$ ground state of N_2^+ is presented. Finally, suggestions for future research are made.

Part I. The Photoemission Experiment

II. Background

In this section a brief description of the physical principles needed to understand excitation, dissociative excitation, and photoemission cross section measurements is given. Specifically, these cross sections are defined, the differences encountered between atomic and molecular targets are explained, the polarization and anisotropy of the emitted radiation is considered, and the relationship of all these quantities to laboratory measurements is presented. A more extensive discussion of the definitions and descriptions presented here can be found in the recent review articles by (Filippelli *et al.*, 1994 and van der Burgt *et al.*, 1989).

The following two processes are considered:



where A and B can be atoms or molecules. In addition, in process (2.2) the reaction may be generalized to include other reaction products (e.g. B^+ , B^* etc.). Process (2.1) is an example of an electron impact excitation followed by photon emission. Process (2.2) describes a process commonly referred to as electron impact dissociative excitation, followed by photon emission. The main focus of this work is on dissociative excitation; processes of type (2.1) were mainly used for normalization. However, the main principles described here are common to both processes.

Excitation, dissociative excitation and photoemission cross sections

The total cross section, $\sigma_{x,j}(E)$ for the direct production of atoms, molecules,

or molecular fragments X in an excited state "j" via electron impact on a gas of atoms or molecules initially in the ground state can be obtained from (Filippelli *et al.*, 1994):

$$n_g j_e \sigma_{X,j}(E) + \sum_{i>j} X_i A_{ij} = \sum_{k<j} X_j A_{jk} \quad (2.3)$$

where n_g is the target gas number density, j_e is the electron flux (the number of electrons per second crossing a unit area perpendicular to the electron beam), E is the electron beam energy, X_j is the mean number of species X in state "j" per unit volume, and A_{ij} refers to the Einstein coefficient for spontaneous decay from state "i" to state "j". Generally, more than one atomic or molecular fragment results from electron impact on a target (more than one channel is available to absorb the increase in internal energy) and many final states are possible for each product, hence the necessity of the labels for the desired species "X" and state "j". Equation (2.3) is valid regardless of whether the species "X" results from excitation or dissociative excitation; in the former case $\sigma_{X,j}(E)$ is called an excitation cross section, in the latter case, a dissociative excitation cross section.

Equation (2.3) expresses the detailed balance between the direct production (*i.e.* no intermediate states) of species X in state "j" together with the cascade from all higher lying levels "i" which can radiatively decay into state "j" whose sum gives the total rate at which X_j is populated, and the spontaneous decay from state "j" to all lower accessible states "k" which is the total rate at which state "j" is depopulated. Under equilibrium conditions these two rates are equal which results in the steady state population, X_j which can be measured by monitoring the intensity of emissions from the spontaneous decay of X_j to lower accessible states.

In the case that there is no cascade contribution to X_j and only one lower

accessible state "k" equation (2.3) becomes

$$n_g j_e \sigma_{jk}(E) = X_j A_{jk} \quad (2.4)$$

where $\sigma_{jk}(E)$ is known as the photoemission cross section for the $j \rightarrow k$ transition. It represents the probability that a collision between the electron and the target eventually gives rise to a photon resulting from the transition from excited state "j" to the lower state "k".

Differences between atoms and molecules

The definitions given above for the excitation, dissociative excitation, and photoemission cross sections can be applied when the emission is resolvable into individual lines as is often the case when the sources of the emission are atoms (ignoring the ionization continuum which we are not concerned with here). However, when the sources of the emission are molecules, because of the nature of molecular spectra the emission is most often not resolvable (with useful intensity) into individual emission lines. Therefore, in the case of molecular emission, along with the definition of the photoemission cross section previously given the following rule becomes necessary (Filippelli *et al.*, 1994).

$$\sigma_{j\nu',k\nu''}(E) = \sum_{J',J''} \sigma_{j\nu'J',k\nu''J''}(E) \quad (2.5)$$

where $j\nu'J'$ are the electronic, vibrational, and rotational quantum numbers of the initial state and $k\nu''J''$ are the electronic, vibrational, and rotational quantum numbers of the final state and the sum is over all possible transitions, $J' \rightarrow J''$, $j\nu' \rightarrow k\nu''$ fixed, that make up the $(j\nu',k\nu'')$ band. Equation (2.5) is the definition of the photoemission cross section for a single molecular vibrational band consisting of many individual closely spaced lines, each of which results from a change in the total angular momentum (predominantly

rotational) of the molecule.

Kinematics

It may be useful to present briefly the kinematics of the electron molecule dissociative excitation process. Because the maximum electron impact energy was not too high, (400 eV) and the mass of even the lightest molecule studied (NF_3) is approximately 130,000 times the mass of the electron, the amount of kinetic energy transferred to the molecule in the collision is negligible (about 10 meV maximum at 400 eV impact energy). Therefore, virtually all the energy lost by the electron goes into raising the internal energy of the parent molecule. If the excited state to which the molecule is raised is unstable (repulsive), the molecule dissociates. Upon dissociating, the internal energy of the parent molecule is shared between the internal energy and increased kinetic energy, ignoring center of mass motion, of the products. It is impossible to know how much energy is transferred to the kinetic energy of the products without knowing the shapes and positions of the potential energy

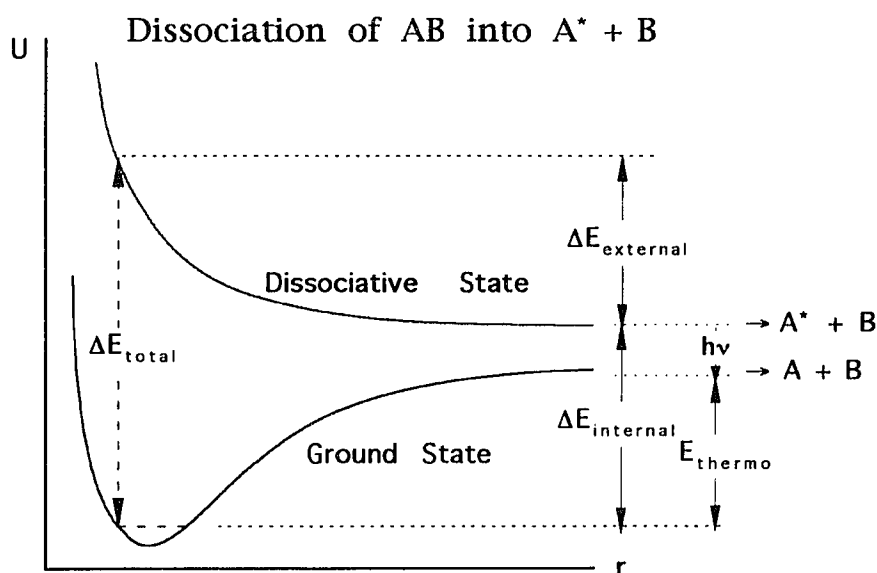


Figure (2.1)

curves (or surfaces) of the ground and excited states of the parent molecule involved in the dissociation. The dissociation process for the simple case of a diatomic molecule is illustrated in figure (2.1) above. The vertical line labeled " ΔE_{total} " in the figure represents the amount of energy obtained by the molecule from the incident electron. The details of how the excess internal energy of the molecule is converted into fragment kinetic energy and fragment internal energy are also displayed in figure (2.1). As shown, $\Delta E_{\text{total}} = \Delta E_{\text{external}} + \Delta E_{\text{internal}}$, where $\Delta E_{\text{external}}$ is the kinetic energy transferred to the fragments. Also, $\Delta E_{\text{internal}} = E_{\text{thermo}} + h\nu$, where E_{thermo} is the heat of formation (dissociation energy), obtained from thermochemical tables (Chase Jr. *et al.*, 1985) and $h\nu$ is the energy of the emitted photon, which is subsequently detected. Because the location of the line labeled " ΔE_{total} " in figure (2.1) is not unique, there is a spread in the amount of kinetic energy transferred to the fragments. At the minimum energy for the appearance of the emission, the energy of the incident electron equals ΔE_{total} ; *i.e.*, the incident electron comes to rest after the collision. Therefore, according to the equation $E_{\text{thresh}}^{\text{meas}} = E_{\text{thermo}} + h\nu + \sum E_{\text{ext}}^{\text{min}}$ the minimum amount of kinetic energy transferred to the fragments can be obtained by taking the difference between the measured threshold energy and the calculated minimum energy (thermochemical plus spectroscopic) for the appearance of the emission, where $E_{\text{thresh}}^{\text{calc}} = E_{\text{thermo}} + h\nu$. In practice the dissociation channel is obtained from $E_{\text{thresh}}^{\text{meas}}$ and a reasonable estimate of $\sum E_{\text{ext}}^{\text{min}}$, typically 0 to 2 eV per fragment (Blanks *et al.*, 1987b and Corr *et al.*, 1987).

Properties of the emitted radiation

The photons observed in the experiments in which we measured photoemission cross sections correspond to dipole-allowed transitions. In

addition, experimental conditions were such that each atom or molecule radiated independently from all the others. Therefore the radiation emitted by the gas from each "j" → "k" transition has the same coherence, polarization and anisotropy properties as the radiation emitted by an ensemble of independent dipoles; *i.e.* the radiation is incoherent and has a radiation pattern which is connected to its polarization through the use of the classical dipole radiation law (Filippelli *et al.*, 1994). Because it is assumed that the exciting electron beam is unpolarized and the atomic or molecular targets have no preferred orientation (before impact) the radiation pattern is cylindrically symmetric, with the electron beam as the symmetry axis, and all directions in a plane perpendicular to the electron beam are equivalent. Three parameters are generally needed to completely characterize the radiation, but because of the cylindrical symmetry we need only two, a customary choice being the "j" → "k" intensities per unit solid angle polarized along both symmetry axes and measured in a plane perpendicular to the electron beam, $I_{jk}^{\parallel}(90^{\circ})$ and $I_{jk}^{\perp}(90^{\circ})$ (see figure 2.2 below). From a measurement of $I_{jk}^{\parallel}(90^{\circ})$ and $I_{jk}^{\perp}(90^{\circ})$ the polarization P_{jk} , defined by (Filippelli *et al.*, 1994)

$$P_{jk} = \frac{I_{jk}^{\parallel}(90^{\circ}) - I_{jk}^{\perp}(90^{\circ})}{I_{jk}^{\parallel}(90^{\circ}) + I_{jk}^{\perp}(90^{\circ})} \quad (2.6)$$

is immediately obtained. Also, according to the equation

$$I_{jk}(\theta) = \frac{I_{jk}}{4\pi} \left[\frac{1 - P_{jk} \cos^2(\theta)}{1 - P_{jk}/3} \right] \quad (2.7)$$

(Filippelli *et al.*, 1994), the total intensity $I_{jk}(\theta)$ can be obtained from a measurement of the polarization P_{jk} and the intensity at the angle θ , where θ is the angle between the electron beam and the direction of observation.

Equation (2.7) gives the relation between the anisotropy and the

Electron Beam (Quantization) Axis

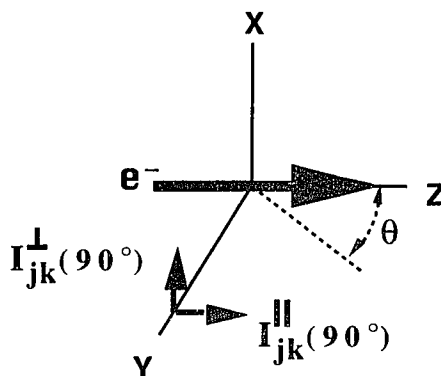


Figure (2.2)

polarization of the emitted radiation. All emissions were monitored at a right angle ($\theta=90^\circ$) to the electron beam. In addition, all emissions were assumed to be unpolarized and therefore isotropic. The justification for this is based on the following discussion.

Measurements of the polarization of ultraviolet (UV) and vacuum ultraviolet (VUV) radiation emitted by atomic or molecular fragments following dissociative excitation are rare; when made the emissions were found to be only slightly polarized ($|P| \leq 0.25$) (Becker *et al.*, 1980 and Malcolm *et al.*, 1979). In addition, the upper limits of the polarization values, ± 0.25 were found only near the threshold energies for the appearance of the emissions; at energies of 100-200 eV, polarization values typically were much smaller. These findings, although not free from ambiguity, are not inconsistent with theoretical treatments of the problem. (Van Brunt *et al.*, 1968) gives two criteria for obtaining polarized emissions following dissociative excitation: (1) a non-uniform distribution in the orientation of dissociation products, and (2) a non-statistical distribution of the magnetic sublevels in the fragment excited states. In general, these conditions can be satisfied when the dissociation proceeds through a single dissociative (repulsive) excited state of the parent

molecule. It is believed the reason for not obtaining polarized emissions following dissociative excitation, especially in the VUV and below, is the breakdown of the second condition above, due to the fact that many repulsive states of different symmetries contribute to the dissociation (van der Burgt *et al.*, 1989).

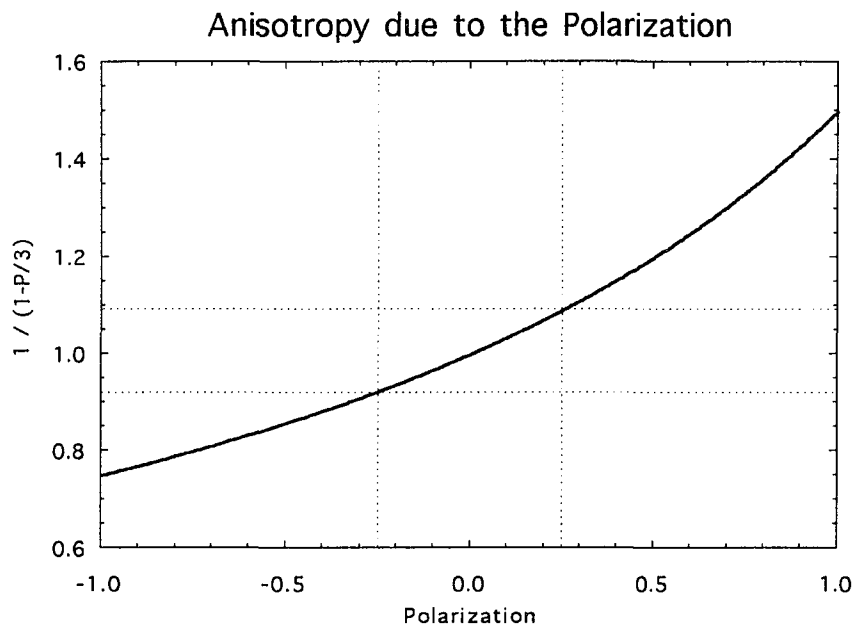


Figure (2.3)

Finally, figure (2.3) above shows the anisotropy $\left. \frac{1 - P \cos^2(\theta)}{1 - P/3} \right|_{\theta=90^\circ}$ in the radiation emitted in a plane perpendicular to the electron beam, caused by the polarization of the emitted radiation. Because the polarization is not measured, the anisotropy which is caused by the polarization is not known. Therefore, an uncertainty, in addition to the statistical and instrumental uncertainties, in the measured photoemission cross sections arises out of the fact that the polarization is not measured. However, as shown in figure (2.3), for $|P| \leq 0.25$ the error from assuming a polarization of zero is less than 10%. In addition, for cross section measurements with an uncertainty of 20% when polarization effects are ignored, the additional uncertainty arising from the inclusion of

polarization effects is less than 2% and is therefore negligible.

Relation to laboratory measurements

In a typical experiment, radiative decay into only one lower lying state $X_j \rightarrow X_k + \gamma_{jk}$ which can either be the ground state or another excited state is observed at any one time. The total number of photons emitted in all directions per unit time and volume, $\Phi_{jk}^{\text{tot}}(E)$, due to this decay is given by

$$\Phi_{jk}^{\text{tot}}(E) = j_e n_g \sigma_{jk}(E) = X_j A_{jk}, \quad (2.8)$$

where all other quantities have been defined previously. The first equality of equation (2.8) contains only quantities measurable in the laboratory and therefore provides a method for obtaining photoemission cross sections. There is however, one additional definition needed. Since the excited state population, X_j appearing in equation (2.8) necessarily includes the cascade contribution from higher excited states as well as the population due to the direct excitation of state "j" the photoemission cross section which appears is called the apparent cross section for the $j \rightarrow k$ transition and, as such, will be labeled $\sigma_{jk}^a(E)$. In order to obtain the corresponding photoemission cross section, $\sigma_{jk}(E)$ the cascade contribution to X_j must either be previously known or measured separately. Likewise, to obtain the corresponding excitation or dissociative excitation cross section for the direct excitation of state "j" either all photoemission cross sections originating from state "j" must be measured or all the optical branching ratios to all accessible lower states must be known.

Since it is not feasible to measure the total volume emission rate, $\Phi_{jk}^{\text{tot}}(E)$, which would require monitoring the intensity in all directions, the intensity per unit solid angle in a given direction is measured instead and equation (2.7) is used to obtain the total intensity. However, since we are assuming a polarization of zero, the radiation is isotropic and the result is:

$$\Phi_{jk}(\theta, E) = \frac{1}{4\pi} j_e n_g \sigma_{jk}^a(E) \quad (2.9)$$

Equation (2.9) serves as the starting point for our photoemission cross section measurements. It contains only quantities directly measurable in the laboratory.

III. Experimental Considerations

Overview of the Method

Electron impact photoemission cross sections were measured using the optical method in the crossed-beam geometry in which a collimated beam of relatively monoenergetic electrons intersects an atomic or molecular gas beam from an effusive source *under single collision conditions*. The intensity of a given atomic line or molecular band excited by the collision is measured as a function of the electron energy using a monochromator-photon detector combination. The resulting relative optical excitation functions were put on an absolute scale by calibrating our apparatus using well known benchmark cross sections.

Apparatus and Procedure

A schematic diagram of the apparatus is shown in figure (3.1). The experiment is housed in a stainless steel vacuum chamber evacuated to a base pressure of approximately 1×10^{-7} Torr by a Sargent Welch model 3134 turbomolecular pump backed by a Sargent Welch model 8821 mechanical pump. The gas beam was formed by effusing the gas through a multicapillary nozzle. The shape and flux of the beam were determined by the pressure behind the nozzle (the "pushing pressure") and the geometry of the nozzle. The pressure was controlled by a Granville Phillips model 203 precision leak valve and monitored by an MKS capacitance manometer model PDR-C-1B. In these experiments pushing pressures ranged from 0.1-0.2 Torr, which resulted in effusive flow conditions, to 1 Torr where the detected emission intensity increased more than linearly with pressure. A pushing pressure of 1 Torr resulted in a background pressure of about 5×10^{-5} Torr, depending on the target gas used. The nozzle consisted of approximately 50 individual

hypodermic needles of inner diameter approximately 0.020" cut to a length of 1/2" which were fitted into a 1/4" i.d. cylindrical fitting and attached to the gas inlet port by a Teflon

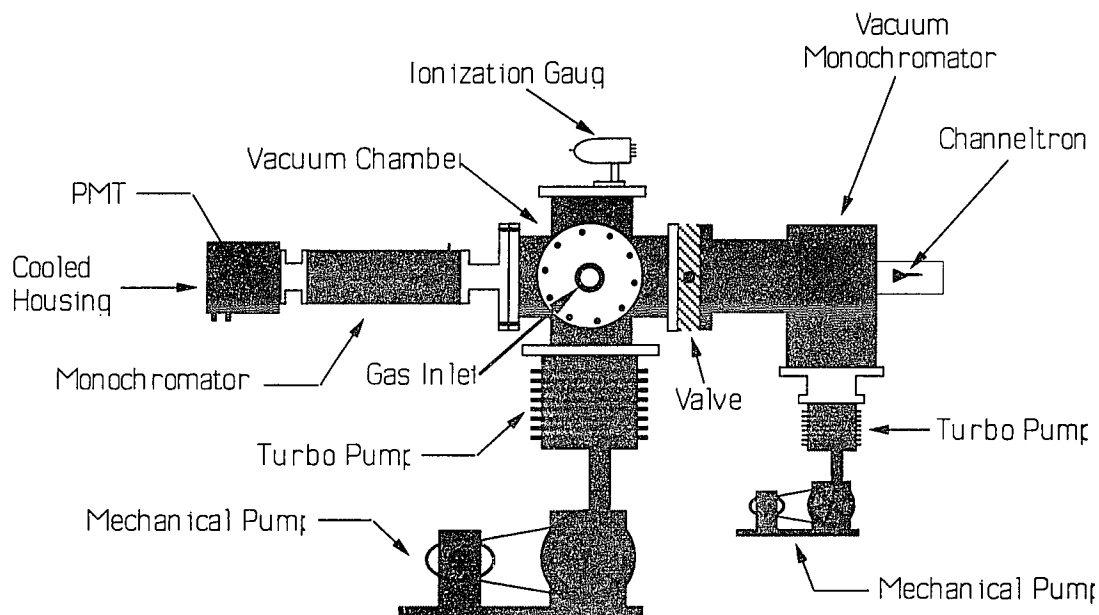


Figure (3.1)

tube and standard Swagelok fittings. The small aspect ratio (diameter/length) and large number of individual capillaries used to form the nozzle resulted in a gas beam of high forward directionality (Giordmane *et al.*, 1960). The impact radiation is observed perpendicular to the plane formed by the electron beam and gas beam. This plane, in turn, is oriented at 45° with respect to the entrance slits of the monochromators to ensure detection free of instrumental polarization effects.

The electron beam was designed to have a high current down to as low an energy as possible in order to measure cross section thresholds with high accuracy. Therefore, no energy analyzer was used. The electron beam was formed using a bare tungsten filament as the source, which was resistively heated by a direct current between 2 and 2.5 Amperes. Four or five aperture

lenses were used (the electron gun was modified during the course of these experiments) for focusing and collimation as shown in figure (3.2). Typical

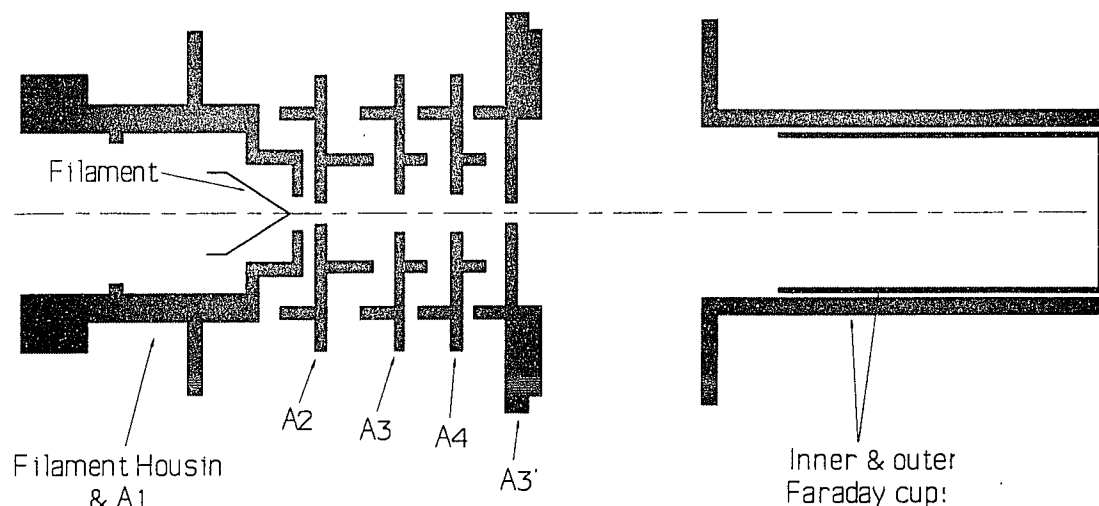


Figure (3.2)

electron beam currents were $120\mu\text{A}$ at 100 eV with a FWHM spread of about 0.75 eV. The electrons were collected and the current was measured using a two element, coaxial geometry Faraday cup as shown. With this arrangement beam divergence as well as total current could be measured. In order to prevent electrons from backscattering into the interaction region, the inner cup was biased slightly positive with respect to the outer cup which was kept at ground potential. In order to minimize secondary electron formation and reduce stray light the last three lens elements of the electron gun, the gas nozzle, the inner Faraday cup as well as the entire inner wall of the vacuum chamber were coated with black soot (Miller Jr. *et al.*, 1987)

As shown in figure (3.1), two independent monochromator-photon detector systems were used to disperse and detect the emitted radiation. Each system observed emissions at right angles to the plane formed by the electron and gas beams. The wavelength range of the emissions determined which system was used. Radiation in the visible and near ultraviolet, from approximately 250 to

800 nm first passed through a sapphire window and was then dispersed with a Bausch and Lomb double-grating monochromator and detected by a Hamamatsu model R955P photomultiplier tube (PMT). In order to decrease thermal noise, the PMT was placed inside a thermoelectrically cooled housing which maintained a temperature of approximately -40° C. The Bausch and Lomb monochromator had an operating range between 2000 and 8300Å and was equipped with 3 sets of fixed slits giving resolutions of 2, 0.5 and 0.2 nm (FWHM's) respectively. Radiation in the vacuum ultraviolet (VUV), from approximately 50 to 250 nm was dispersed with a Minuteman vacuum monochromator model 302-VM and detected with a Galileo Electro Optics model 4039C channel electron multiplier (channeltron). The Minuteman monochromator had a holographic grating whose operating range was between 50 and 250 nm and was equipped with variable slits controlled by a micrometer. Because radiation in the VUV (below approximately 180 nm) is absorbed by the air, the vacuum monochromator and channeltron were kept under vacuum using a separate turbomolecular and mechanical pumping station. The operating pressure in this section of the apparatus was approximately 5×10^{-7} Torr.

Both the PMT and channeltron detectors were used in the photon counting mode. Their output consisted of pulses which, after suitable amplification and discrimination were counted by an Apple IIe driven multichannel scalar (MCS). The MCS accumulated the pulses received within a predetermined time interval (the dwell time) in a single channel; pulses received during consecutive dwell times were placed in consecutive channels. The MCS was used in conjunction with either a programmable power supply that ramped the electron beam energy or an asynchronous motor attached to one of the monochromators that ramped the monochromator wavelength setting. The

resulting data consisted of a table of the numbers stored in each channel of the MCS (which were proportional to the emission intensity) versus either the electron beam energy (energy scan) or the wavelength setting (wavelength scan). The data were stored on floppy discs which could be read by either an Apple IIe, Macintosh or IBM compatible computer.

The Interaction region

As shown in figure (3.3), the electron beam, gas beam, and optical axis are mutually perpendicular to each other. The interaction region is determined by the intersection of the electron and gas beams and when detecting emissions from electric dipole allowed transitions (typical lifetimes of 1-100 ns) coincides with the photon emission region. The optical axis is defined by the line originating at the center of the interaction region and terminating at the photon detection system.

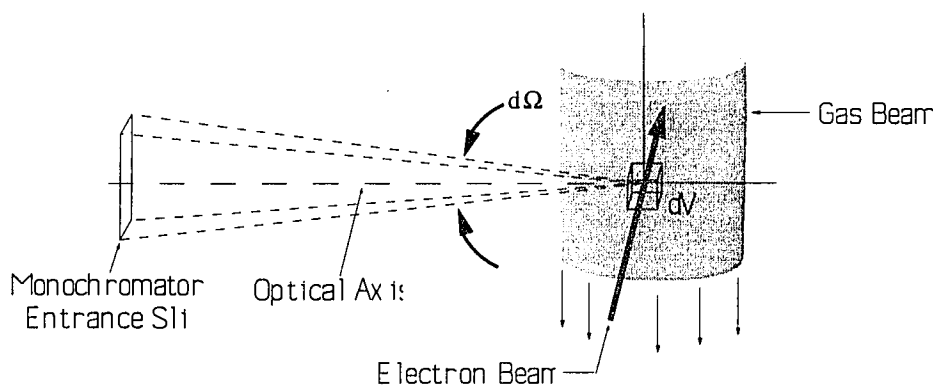


Figure (3.3)

Electron beam energy spread

As mentioned, the electron beam is not strictly monoenergetic, but has an energy spread of approximately 0.75 eV. Because of this, equation (2.9) should actually be modified to read

$$\Phi_{jk}(\theta, E) = (1/4\pi) \int j_e(E') n_g \sigma_{jk}^a(E') dE'; \quad (3.1)$$

i.e., the photoemission cross section, measured at a nominal energy set by the voltage difference applied between the electron gun cathode and anode and corrected for the contact potential that is actually obtained, corresponds to an average over the electron beam energy distribution. The electron flux density appearing in equation (3.1), $j_e(E')$ should actually be written as $j_e(\bar{r}', E')$, but because the energy spread of the electron beam originates at the source (cathode), $j_e(\bar{r}', E')$ can be factored into the product $j_e(\bar{r}')g(E - E')$ where $g(E - E')$ is a Gaussian with mean energy E and unit area (Filippelli *et al.*, 1994). Not including resonances, $\sigma_{jk}^{app}(E)$ can be approximated by a straight line over this energy range. Therefore, after integrating equation (3.1) over dE' we again obtain equation (2.9), *i.e.*, the energy at which the photoemission cross section is obtained is the mean energy of the electron beam.

Detection sensitivity of the photon detection system

The monochromator-photon detector combinations used in these experiments have a detection efficiency that depends on the wavelength and polarization of the incident radiation. The detection efficiencies of the monochromator can be written as $k_{||}(\lambda)$ and $k_{\perp}(\lambda)$ for light polarized parallel and perpendicular to the grooves of the diffraction grating and the detection efficiency of the photon detector can be written as $E_D(\lambda)$, where we assume that the photon detector is polarization insensitive. Therefore, the signal obtained at the detector can be written as $S_D = E_D(\lambda)[k_{||}(\lambda)I_{||} + k_{\perp}(\lambda)I_{\perp}]$ where $I_{||}$ and $I_{\perp}$ are the incident light intensities polarized parallel and perpendicular to the long axis of the monochromator entrance slit (and therefore also to the grooves of the grating inside). However, our photon detection systems were rendered polarization insensitive by orienting the

vertical axes of the monochromator entrance slits at a 45° angle to the plane formed by the electron beam and optical axis (Clout *et al.*, 1969, Filippelli *et al.*, 1994, and van der Burgt *et al.*, 1989). (At this angle $I'_{\parallel} = I'_{\perp} = \frac{1}{2}(I_{\parallel} + I_{\perp})$ so that $S_D = E_D(\lambda)[k_{\parallel}(\lambda) + k_{\perp}(\lambda)]\frac{1}{2}(I_{\parallel} + I_{\perp})$.) This allows us to make a comparison of emission intensities from different sources without regard to their respective polarizations. However, this process does not eliminate the wavelength sensitivity of our photon detection systems which has to be known, at least in relative terms, in order to compare emission intensities at different wavelengths.

Signal incident on the monochromator

The signal incident on the monochromator coming from the interaction region is given by

$$S_{M_{jk}}(E) = \iint \Phi_{jk}(\theta, E) d\Omega(\vec{r}') d\vec{r}' = \sigma_{jk}^{app}(E) \iint j_e(\vec{r}') n_g(\vec{r}') d\Omega(\vec{r}') d\vec{r}', \quad (3.2)$$

where the second equality follows from equation (2.9) and the energy spread in the electron beam is accounted for according to the previous discussion. Since the distance between the monochromator entrance slit and the center of the interaction region (geometrical center of the vacuum chamber) is approximately 200 mm, while the diameter of the interaction region (which is determined by the diameter of the electron beam) is approximately 2 mm, the variation of the solid angle subtended by the entrance slit over the interaction region is negligible and the $d\Omega(\vec{r}')$ integration can be trivially performed to yield finally

$$S_{M_{jk}}(E) = \sigma_{jk}^{app}(E) \Delta\Omega \int j_e(\vec{r}') n_g(\vec{r}') d\vec{r}', \quad (3.3)$$

where $\Delta\Omega$ is the average solid angle subtended by the monochromator entrance slit at the interaction region. Equation (3.3) directly illustrates how

the measured emission intensity depends on the electron beam-gas beam overlap.

Signal obtained from the photon detector

The signal at a given monochromator wavelength setting, λ_{set} consists of radiation that is transmitted by the monochromator in an interval around λ_{set} determined by the monochromator slit function, $f(|\lambda - \lambda_{\text{set}}|/\Delta\lambda)$. $\Delta\lambda$, known as the resolution, is determined by the slit widths. The slit function, normalized to unity at $\lambda = \lambda_{\text{set}}$, gives the relative transmission probability when $\lambda \neq \lambda_{\text{set}}$. Therefore, the signal incident on the photon detector contains a convolution of the signal entering the monochromator and the monochromator slit function. In addition, the overall transmission efficiencies of the monochromator, (written as $k_M(\lambda)$ because the polarization sensitivity has been eliminated), quartz window (if present), and photon detector determine the signal obtained from the photon detector. The detector signal, $S_D(\lambda_{\text{set}})$ (photons/s) at a given monochromator wavelength setting is given by

$$S_D(\lambda_{\text{set}}) = k_M(\lambda_{\text{set}})k_D(\lambda_{\text{set}})t_w(\lambda_{\text{set}})\int S_{M_{jk}}(E)f(|\lambda - \lambda_{\text{set}}|/\Delta\lambda)d\lambda \quad (3.4)$$

where $k_D(\lambda)$ and $t_w(\lambda)$ are the transmission efficiencies of the photon detector and quartz window and the small variations of $k_D(\lambda)$ and $t_w(\lambda)$ over the range $\Delta\lambda$ have been neglected.

In order to evaluate the integral in equation (3.4) both the slit function and the wavelength dependence of the cross section must be known. In the results that follow a simple triangular slit function, $f(\hat{\lambda}) = 1 - |\hat{\lambda}|/\Delta\lambda$ where $\hat{\lambda} = \lambda - \lambda_{\text{set}}$ has been assumed and, as mentioned, $\Delta\lambda$ ranged from 0.2 to 2 nm. The wavelength dependence of the cross section, due to the natural lifetime of the excited state, is a Lorentzian with a typical FWHM for dipole allowed

transitions of 1 to 2 $\times 10^{-5}$ nm at a wavelength of 800 nm. Therefore, this wavelength dependence is negligible and a delta function

$\sigma_{jk}^{app}(E) \rightarrow \sigma_{jk}^{app}(E)\delta(\lambda - \lambda_{jk})$ will be used. With these assumptions, the integral in equation (3.4) can be performed, yielding

$$S_D(\lambda_{set}) = k_M(\lambda_{set})k_D(\lambda_{set})t_w(\lambda_{set})S_{M_{jk}}(E)f(|\lambda_{jk} - \lambda_{set}|/\Delta\lambda). \quad (3.5)$$

When the intensity of an atomic line is measured, the monochromator wavelength setting, λ_{set} is held fixed. Therefore assuming $\lambda_{set} = \lambda_{jk}$ and substituting for $S_{M_{jk}}(E)$ the signal becomes

$$S_D(\lambda_{jk}) = k_M(\lambda_{jk})k_D(\lambda_{jk})t_w(\lambda_{jk})\sigma_{jk}^{app}(E)\Delta\Omega \int j_e(\vec{r}')n_g(\vec{r}')d\vec{r}'. \quad (3.6)$$

$S_D(\lambda_{jk})$ appearing in equation (3.6) multiplied by Δt , the amount of time per channel spent detecting photons is a single data point: that is, $S_D(\lambda_{jk})\Delta t$ gives the number stored in each channel of the MCS at the end of a data taking period.

When the wavelength is scanned across an atomic line, as when measuring an emission spectrum from an excitation or dissociative excitation process, the *total* signal (*i.e.*, the signal summed over the appropriate number of channels) is proportional to:

$$T_D^{\Delta\lambda}(X_{j \rightarrow k}) = k_M k_D t_w \sigma_{jk}^{app}(E) \Delta\Omega \Delta\lambda \int j_e(\vec{r}')n_g(\vec{r}')d\vec{r}'. \quad (3.7)$$

The $T_D^{\Delta\lambda}(X_{j \rightarrow k})$ appearing above is not the number stored in each channel of the MCS. The number stored in each channel of the MCS is determined by another parameter, the change in monochromator wavelength setting per channel, and since it is not necessary for our purposes it will not be given here. Note that for clarity the wavelength dependence of the transmission efficiencies k_M , k_D , and t_w has been omitted. In this case (wavelength is scanned) they should be evaluated at $\bar{\lambda}_{jk}$, the average wavelength detected.

When detecting the emissions from a molecular band, the wavelength is always scanned, either when doing a spectral survey or when measuring the intensity as a function of electron beam energy. Therefore an equation analogous to equation (3.7) applies:

$$T_D^{\Delta\lambda}(jv', kv'') = k_M k_D t_w \sigma_{jv', kv''}(E) \Delta\Omega \Delta\lambda \int j_e(\vec{r}') n_g(\vec{r}') d\vec{r}', \quad (3.8)$$

where the only change from equation (3.7) is in the cross section,

$\sigma_{jv', kv''}(E) = \sum_{J', J''} \sigma_{jv'J', kv''J''}(E)$ which as mentioned, is now the sum of the individual cross sections, for $J'' \rightarrow J'$ that make up the (jv', kv'') band. The $T_D^{\Delta\lambda}(jv', kv'')$ appearing above is the signal summed over the channels of the MCS that encompasses the entire band, and again the explicit wavelength dependence of the transmission efficiencies k_M , k_D , and t_w has been omitted. They should be evaluated at $\bar{\lambda}_{jv', kv''}$, the average wavelength detected.

Normalization and calibration

As mentioned, our photoemission cross sections were put on an absolute scale by comparing them with known benchmark cross sections. Care was taken to measure the unknown cross section and the known cross section under identical experimental conditions. The normalization was done at a single electron beam energy, typically 100 or 200 eV where polarization effects are expected to be minimal (Malcolm *et al.*, 1979). In the VUV, we used the 121.6 nm Ly- α emission produced by dissociative excitation of H_2 [$H_2 + e^- \rightarrow 2H + e^- + \text{Ly-}\alpha(121.6 \text{ nm})$]. We used a value of $7.2(\pm 0.6) \times 10^{-18} \text{ cm}^2$ at 100 eV, which is an average of three recent reliable measurements (see table 3.1), for the cross section for this process. Because cross sections corresponding to emissions at different wavelengths were compared, the relative wavelength sensitivity of our photon detection systems had to be known. In addition, because cross sections from different gases and different pushing pressures

were compared, accurate curves of intensity versus pushing pressure had to be measured. The accuracy of our photon detection system calibration and gas number density normalization technique is crucial to the accuracy of our photoemission cross section measurements. Therefore, the detailed method for both of these procedures is the focus of this section. Lastly, the procedure used to calibrate the electron beam energy in the interaction region is described.

Recent Lyman- α emission cross section measurements [$\text{H}_2 + \text{e}^- \rightarrow 2\text{H} + \text{e}^- + \text{Lyman-}\alpha(121.6 \text{ nm})$]	
σ (10^{-18} cm^2)	Reference
7.3 (± 0.7)	(Ajello <i>et al.</i> , 1988)
7.13 (± 0.59)	(Woolsey <i>et al.</i> , 1986)
7.22 (± 1.36)	(Van Zyl <i>et al.</i> , 1985)
7.2 (± 0.6)	Average

Table (3.1)

Wavelength sensitivity of our photon detector systems

The relative wavelength sensitivity of our monochromator-channeltron combination in the VUV (80-170 nm) was measured using a model spectrum of electron impact produced H_2 emissions that was provided to us by Ajello and co-workers (Ajello *et al.*, 1988). The model spectrum consisted of the approximately 70,000 fine structure lines from the Lyman ($\text{B}^1 \Sigma_u^+ \rightarrow \text{X}^1 \Sigma_g^+$) and Werner ($\text{C}^1 \Pi_u \rightarrow \text{X}^1 \Sigma_g^+$) bands and higher members of each Rydberg series ($^1 \Sigma_u^+ n p \sigma$ and $^1 \Pi_u n p \pi$, $n=2,3,4$) as well as the Lyman- α and Lyman- β emission lines, which account for all of the H_2 and H emissions between 80 and 170 nm. The synthetic H_2 spectrum is based primarily on the molecular branching ratio technique of (Mumma, 1972), extended to include simultaneous emissions from multiple upper states. In addition, the synthetic H_2 spectrum used calculated band oscillator strengths and transition probabilities (Allison *et al.*, 1970). It

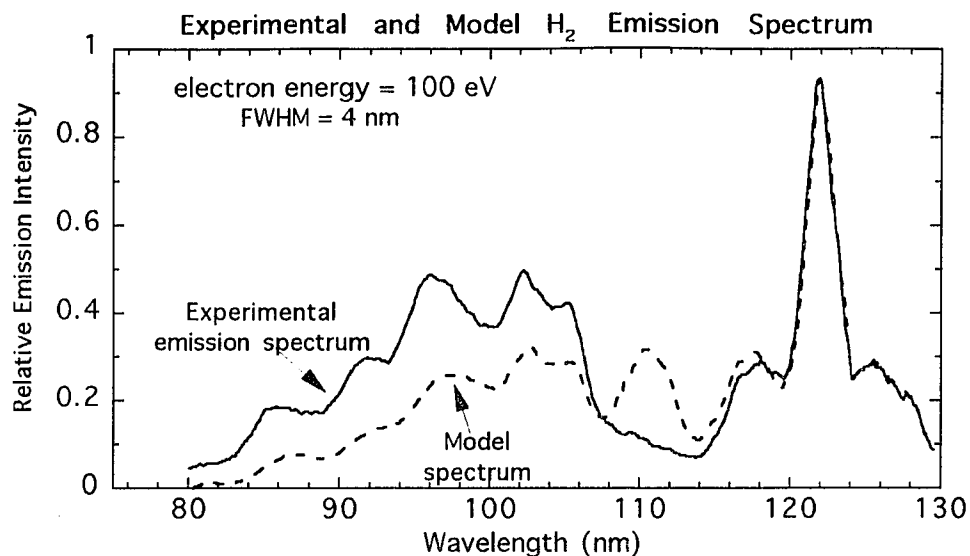


Figure (3.4).

was developed in conjunction with experimental studies of the electron-impact excited hydrogen spectrum of (Ajello *et al.*, 1984, Ajello *et al.*, 1982, and Shemansky *et al.*, 1983), which also served as a check on the model's accuracy. Between 80 and 120 nm the RMS difference between the model and an

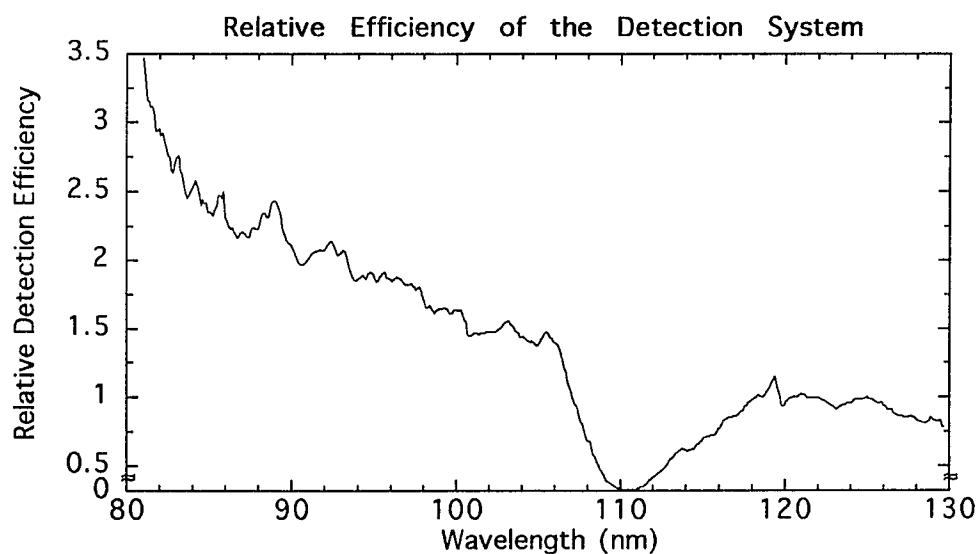


Figure (3.5)

experimental spectrum based on 27 integrated peaks was 10.2% (Ajello *et al.*, 1988). In order to make a comparison with experiment the discrete rotational

line spectrum provided by the model had to be convolved with the monochromator slit function. The results are shown in figure (3.4) for emissions between 80 and 130 nm and an experimental and theoretical resolution of 4 nm. From this we obtained the desired relative wavelength sensitivity, shown in figure (3.5) which was obtained by taking the ratio of the experimental data to the model spectrum.

The relative wavelength sensitivity of our monochromator-PMT combination in the visible (200-800 nm) was measured using a 50 Watt quartz-iodine lamp which provided a near-blackbody spectrum. The color temperature of the lamp was measured using an optical pyrometer and the resulting spectrum calculated using the well known Planck radiation law. Emission from the lamp was not polarized. The resulting relative sensitivity

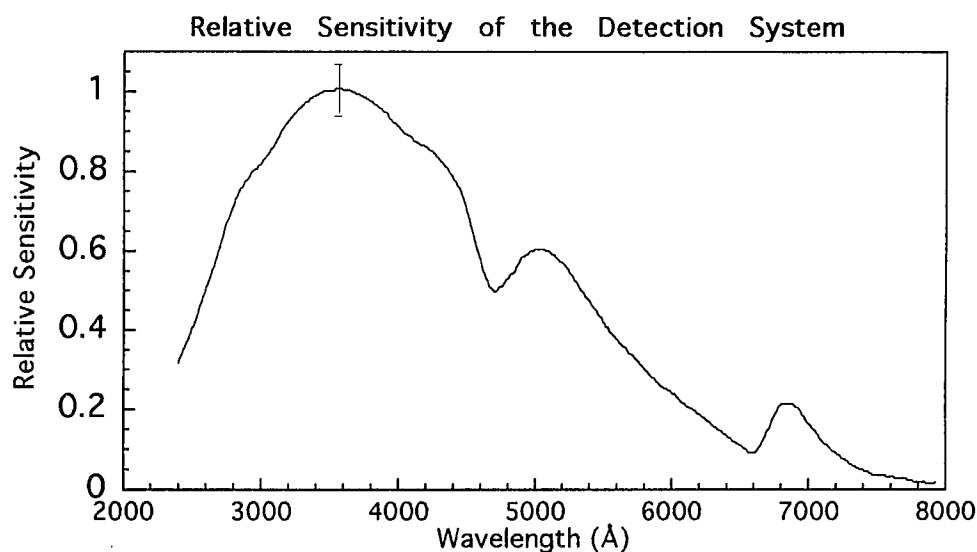
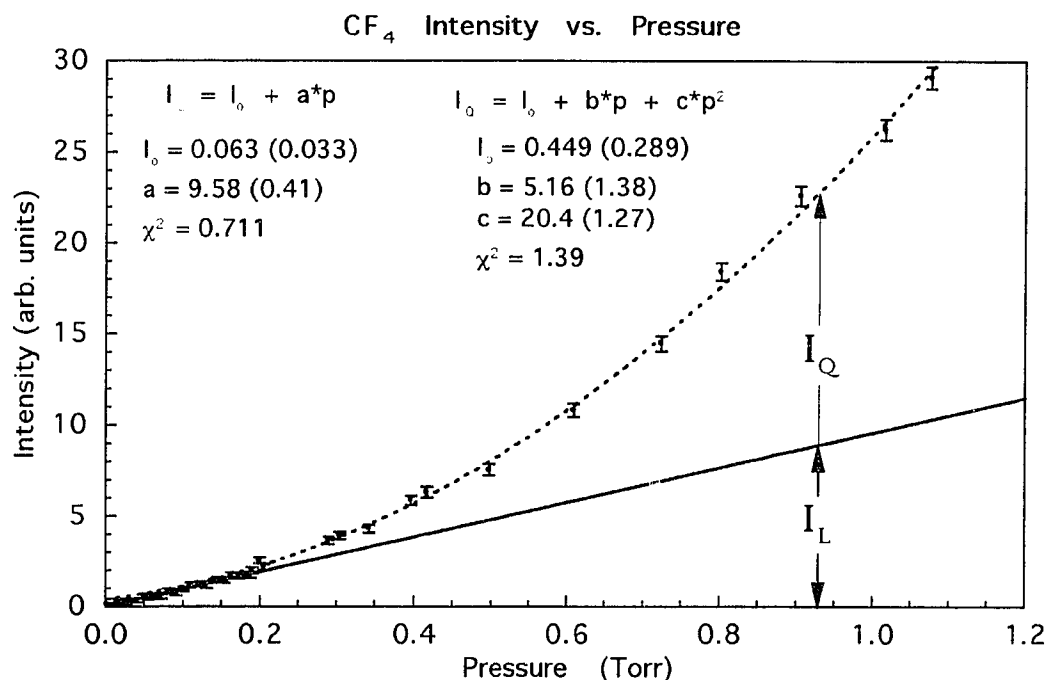


Figure (3.6)

curve from 2500 to 8000 Å is shown in figure (3.6). The error bar represents the $\pm 7\%$ uncertainty due to the uncertainty in the determination of the temperature of the lamp.

Normalization to gas pressure

As mentioned, in order to compare emission intensities from different gases and different pushing pressures, intensity versus pressure curves were measured. An example is shown in figure (3.7) for CF_4 , which shows the intensity (in arbitrary units) normalized to the electron beam current on the y-axis and the pressure behind the nozzle, the pushing pressure, on the x-axis. As shown, a linear fit was applied to the low pressure regime, $P < 0.2$ Torr, and a quadratic fit was applied at higher pressures. In order to achieve usable signal to noise ratios, data had to be taken at pressures well above the linear range; i.e., where the quadratic fit applied. The normalization



procedure consisted of converting the intensity measured at a given pressure to the intensity corresponding to the linear fit extrapolated to the same pressure, $I_{\text{Norm}} = I_{\text{Meas}} (I_L / I_Q)$ as shown in the figure. (Note that the uncertainty in the extrapolated signal, I_L , as determined by varying the

number of points used in the extrapolation procedure, was always less than 5%, and therefore made only a small contribution to the overall uncertainties.) Therefore, The normalized emission intensities, $I_{\alpha m}$ obtained in this way can then be directly compared with each other. Specifically, after normalizing to the gas pressure as described above, the ratio of two signals corresponding to emissions from excited atoms can be obtained from equation (3.6). The result is

$$R = I_X^{\text{Norm}}(\lambda_{jk}) / I_Y^{\text{Norm}}(\lambda_{lm}) = \frac{\epsilon(\lambda_{jk}) \sigma_{X,jk}^{\text{app}}(E) I_e^X P_X}{\epsilon(\lambda_{lm}) \sigma_{Y,lm}^{\text{app}}(E) I_e^Y P_Y} \quad (3.9)$$

where for species X, $I_X^{\text{Norm}}(\lambda_{jk})$ is the normalized detector signal and $\epsilon(\lambda_{jk})$ the combined monochromator-photon detector efficiency at the wavelength λ_{jk} , I_e^X is the electron beam current and P_X is the pushing pressure. The corresponding symbols have the same meaning for species Y. Equation (3.9) relates the ratio of the two emission cross sections, $\sigma_{X,jk}^{\text{app}}(E) / \sigma_{Y,lm}^{\text{app}}(E)$ only to quantities directly measured in the laboratory and therefore can be used to determine, on an absolute scale, an unknown cross section in terms of a known cross section.

The explanation of the above gas normalization procedure is as follows. At low pushing pressures corresponding to gas kinetic mean free paths, $\lambda_g \geq d$ where d is the diameter of an individual hypodermic needle making up the nozzle (Knudsen number $K_n \geq 1$), the conductance of the needle is a constant that depends only on the geometry of the nozzle ($C \propto d/L$ where L is the length of the needle). This regime is known as the molecular flow regime (Roth, 1990). Because the conductance is independent of the pushing pressure the rate of flow of gas through the nozzle is directly proportional to the pressure difference across the ends of the nozzle. The pressure at the nozzle exit is at least an order of magnitude less than the input pressure and therefore can be neglected when calculating throughputs. The throughput, or flux through

the nozzle is directly proportional to the gas number density, n_g in the interaction region. Therefore, in the molecular flow regime the emission intensity, which is directly proportional to the overlap integral, $\int j_e(\vec{r}') n_g(\vec{r}') d\vec{r}'$ is directly proportional to the pushing pressure behind the nozzle. Specifically, the overlap integral becomes $kl_e p$ where k is a constant. As specified, this expression is valid in the molecular flow regime where $\lambda_g \geq d$. The molecular flow regime extends up to 0.1 - 0.2 Torr, depending on the particular gas used. The boundary is signaled by the breakdown of the linear relationship between the emission intensity and the pushing pressure.

When the pushing pressure is increased past this boundary, to the point where $\lambda_g < d$, the conductance of the needle becomes proportional to the pressure difference across the nozzle. Therefore, the rate of flow of gas through the nozzle becomes proportional to the pressure difference squared. This regime is known as the viscous flow regime and is signaled by an emission intensity tending to vary as the square of the pushing pressure (Roth, 1990). In addition, there is an intermediate regime separating the molecular and viscous regimes, however this is unimportant for our purposes. The important operation for the gas normalization procedure is the extrapolation of the molecular flow or linear regime to the pressures outside this regime which are used when data are taken.

Electron Beam Energy Calibration

Accurate knowledge of the mean kinetic energy with which electrons impact on our gas targets, the impact energy, is crucial in the determination of the minimum energy required to produce a specific emission, known as the threshold or onset energy. The impact energy is nominally controlled and measured by the voltage applied between the cathode and anode of the

electron gun. However, because of contact potential effects the measured and true impact energies will be different (Ashcroft *et al.*, 1976). In extreme cases this difference can be as much as 3 eV. In addition, because conditions at the surface of a material such as an applied coating, an adsorbed monolayer or surface damage caused by electron impact can affect the work function of the material, the difference between the true and measured impact energies can vary with time. In the extreme case, for a target such as BCl_3 , this rate, known as contact potential drift was measured to be as high as 0.6 eV per hour (Gilbert *et al.*, 1990). These difficulties point to the need for an accurate *in situ* method for determining the contact potential difference which can be (and was) applied at frequent intervals. We used the accurately measured 11.03 eV onset of the electron-impact produced $\text{N}_2 \text{ } ^3\Pi_u \rightarrow \text{B}^3\Pi_g$ (2nd positive system) emission at 337.1 nm to calibrate the energy of our electron beam (Finn *et al.*, 1972). Before and after each data acquisition period in which an optical excitation function was measured, either pure N_2 or a mixture of N_2 and the target gas was admitted into the interaction region and the onset for the $\text{N}_2 \text{ } ^3\Pi_u \rightarrow \text{B}^3\Pi_g$ emission measured. Agreement between the two onsets was typically ± 0.2 eV. Using this procedure electron impact energies could be calibrated to within ± 0.3 eV for all target gases with the exception of BCl_3 . In all cases onset energies were measured with an uncertainty of approximately ± 1.5 eV which is the result of the uncertainty in the contact potential and statistical uncertainties.

IV. Results and Discussion

The dissociative excitation of many molecules has been studied in our group using the apparatus and methods discussed. In particular, emission spectra and absolute photoemission cross sections for the simple halogen containing molecules SF_6 , CF_4 , NF_3 , CCl_2F_2 , (Blanks *et al.*, 1987a, Blanks *et al.*, 1987b, Jabbour *et al.*, 1989, Jabbour *et al.*, 1988a, and Rogue *et al.*, 1991), and BCl_3 (Jabbour *et al.*, 1988b)(Jabbour *et al.*, 1988b, Jabbour *et al.*, 1988b, and Gilbert *et al.*, 1990) will be presented. Additional molecules studied include SO_2 , (Miller Jr. *et al.*, 1987), and TEOS (tetra-ethoxysilane) (Ducrepin *et al.*, 1993), but results for these molecules will not be presented here.

Through the identification of specific spectroscopic features, electron impact produced emission spectra were used to identify the dissociation products. For the fluorine containing molecules, two groups of atomic fluorine lines were prominent: resonance lines corresponding to the $2p^4 3s \rightarrow 2p^5$ transitions in the VUV and lines corresponding to the $2p^4 \ 3p \rightarrow 2p^4 3s$ transitions in the visible. For the chlorine containing molecule BCl_3 , atomic boron lines due to the $2s2p^2 \rightarrow 2s^2 2p$ and $2s^2 3s \rightarrow 2s^2 2p$ transitions as well as vibrational bands due to the $\text{BCl} (A^1 \Pi \rightarrow X^1 \Sigma^+)$ electronic transition in the UV were prominent.

After the strongest emission features were identified, the corresponding emission cross sections were measured. Most emission cross sections displayed the typical shape expected from an optically allowed dipole excitation; *i.e.*, a broad maximum at an energy between approximately four and ten times the threshold followed by a slow decline. The unusual shape of the excitation function that occurred for $\text{CCl}_2 \text{F}_2$ was recognized as arising from the opening of a second dissociation channel leading to the same emitting fragments, but

with different threshold energies.

Particular attention was paid to accurately measuring the threshold energies for the emissions that were detected. In favorable cases the threshold energy uniquely determines the dissociation channel; *i.e.*, total versus partial fragmentation of the parent molecule. In all cases, knowledge of the onset energy narrowed the number of possible dissociation channels. For some targets, separate thresholds close together were found which was attributed to the opening of another dissociation channel which produced a higher excited state of the emitting fragment. This higher excited state population contributed to the measured photoemission cross section through the cascade process previously discussed.

Fluorine 3p→3s emissions from SF₆, CF₄, NF₃, and CCl₂F₂

Figure (4.1) shows the emission spectrum between 6000 and 8000 Å

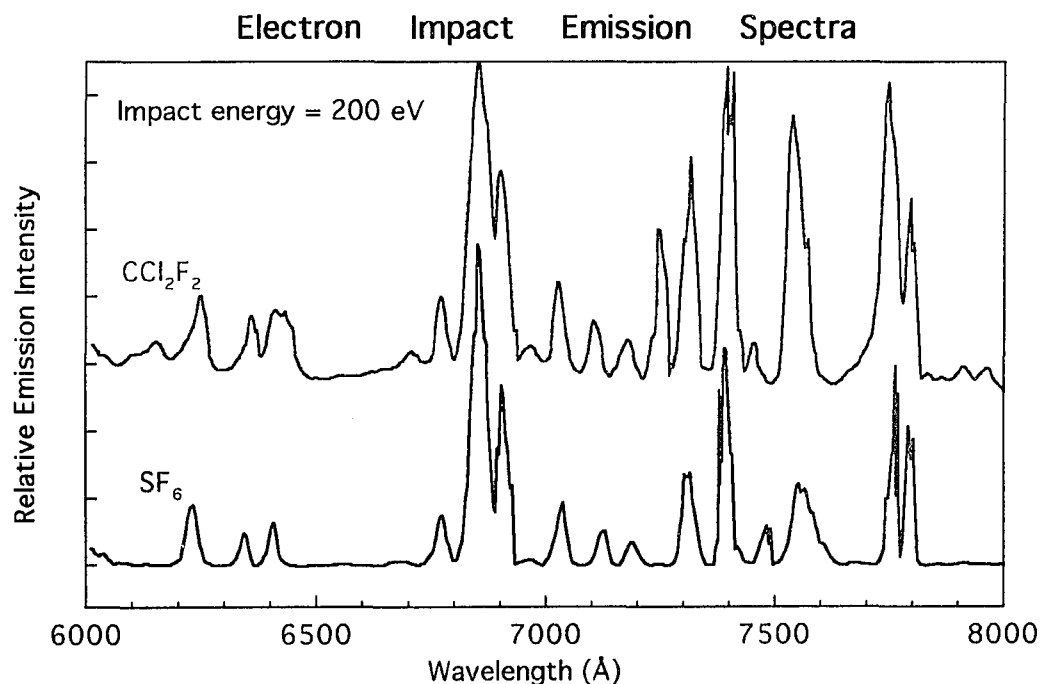


Figure (4.1)

produced by 200 eV electrons incident on SF_6 and CCl_2F_2 . Nearly identical spectra were produced for CF_4 and NF_3 . All the emissions are due to atomic fluorine (FI) $3p \rightarrow 3s(^2,^4P)$ transitions with the exception of three additional lines present in the CCl_2F_2 spectrum which are due to atomic chlorine (CII) $4p \rightarrow 4s$ transitions. Because there are no overlapping FI lines, the most noticeable CII line is at 7257Å. Figure (4.2) shows a partial Grotrian diagram (Bashkin *et al.*, 1975) for FI displaying the $3p \rightarrow 3s$ transition wavelengths as well as the FI resonance transitions ($3s \rightarrow 2p$) (which will be discussed shortly).

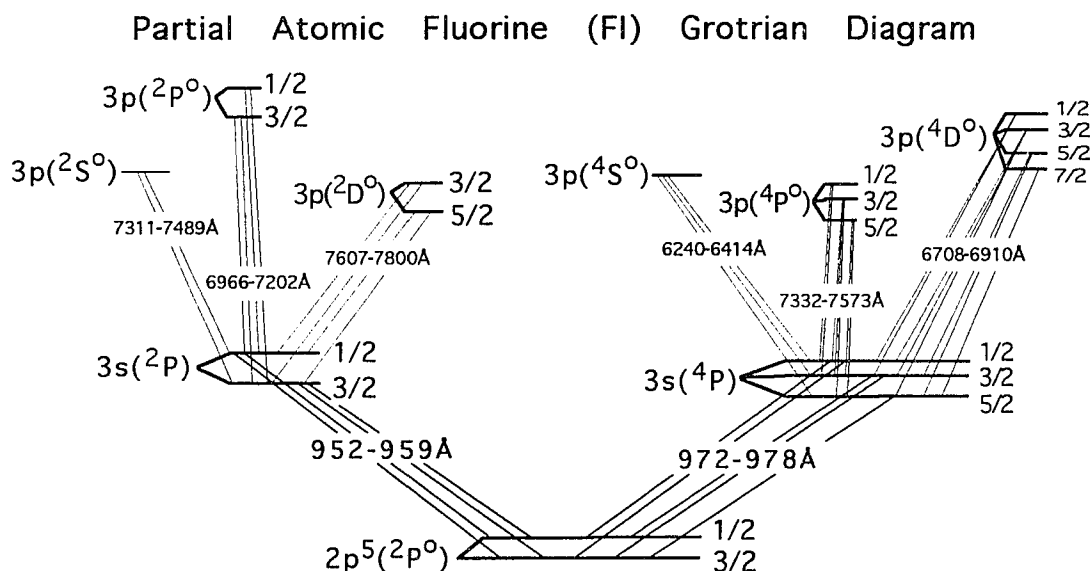


Figure (4.2)

Figure (4.3) shows the absolute photoemission cross sections for the $^4D^o \rightarrow ^4P$ multiplet (between 6700 and 6900 Å) for SF_6 , CF_4 and NF_3 (the corresponding cross section for CCl_2F_2 showed a very similar energy dependence). The $^4D^o \rightarrow ^4P$ multiplet accounts for 36% of the total $3p \rightarrow 3s$ emission cross section at 100 eV impact energy for these three target gases which is also apparent from the similarity of their emission spectra. Note that NF_3 has the largest cross section, followed by CF_4 and SF_6 , and this same order is followed for all the $3p \rightarrow 3s$ transitions. The maximum cross sections occurred at approximately 175

eV for all target gases, which is about four times the measured threshold energy. The maxima were followed by a slow decline. The overall shape of the cross sections indicates that the excited state of the parent molecule from which the emissions originate is reached by an optically allowed transition, as mentioned earlier.

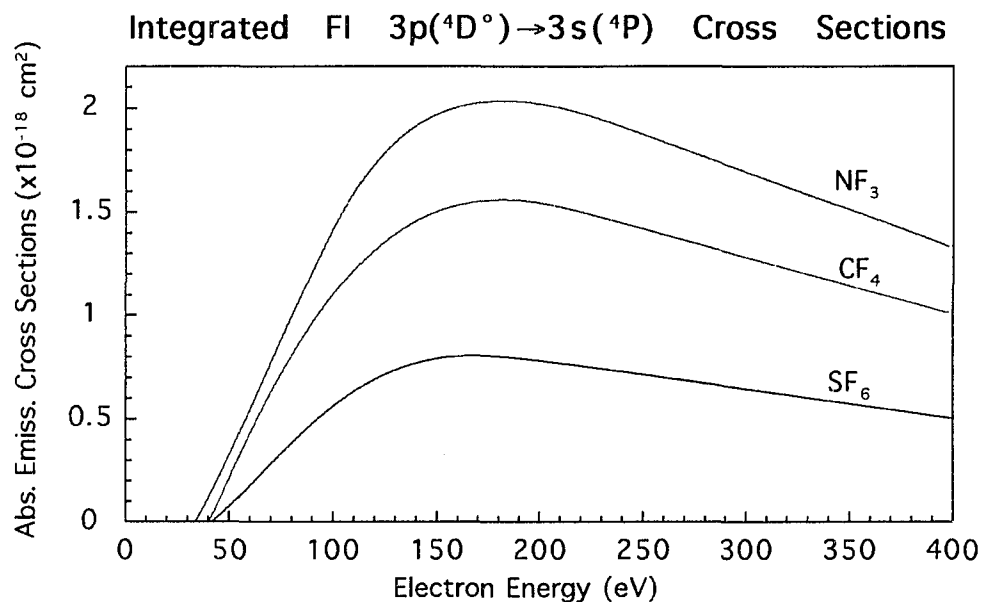


Figure (4.3)

Table (4.1) gives the absolute photoemission cross sections for all observed fine structure components (individual lines) for all four target gases at 100 eV impact energy. The uncertainty for cross sections larger than $1 \times 10^{-19} \text{ cm}^2$ is $\pm 20\%$, for cross sections smaller than $1 \times 10^{-19} \text{ cm}^2$, $\pm 25\%$; and due to the lower sensitivity of our photon detector system, all cross sections above $7500 \text{ \AA}$ have an uncertainty of $\pm 40\%$. In the case of SF_6 , at an impact energy of 200 eV, the sums of all the emission cross sections for transitions that terminate in the $3s^4P$ and $3s^2P$ configurations are $14.8 \times 10^{-19} \text{ cm}^2$ and $6.7 \times 10^{-19} \text{ cm}^2$, respectively. In the case of CCl_2F_2 , at 100 eV impact energy, these sums are $16.2 \times 10^{-19} \text{ cm}^2$ and $7.5 \times 10^{-19} \text{ cm}^2$, respectively. These sums are needed to calculate the $3p \rightarrow 3s$

cascade contribution to the 3s→ 2p emission cross sections in the VUV (see discussion later).

FI Emission Cross Sections, σ_{em}^{app} at 100 eV ($\times 10^{-19}$ cm ²)											
Transition	$\lambda(\text{\AA})$	NF ₃	CF ₄	CCl ₂ F ₂	SF ₆	Transition	$\lambda(\text{\AA})$	NF ₃	CF ₄	CCl ₂ F ₂	SF ₆
⁴ S° → ⁴ P	6240	1.4	1.2	0.9	0.6	² S° → ² P	7311)				
	6349	1.0	0.8	0.6	0.4						
	6413	0.8	0.6	0.4	0.3		}	4.3	3.3	2.4	1.4
	6774	1.1	0.8	0.6	0.4		7332)				
	6795	0.2	0.2	0.1	<0.1		7399	5.3	3.9	2.8	2.1
⁴ D° → ⁴ P	6834	1.6	1.2	0.9	0.6	⁴ P° → ⁴ P	7483)				
	6856	6.1	4.7	3.5	2.5		}	0.9	0.6	0.6	0.3
	6870	1.3	0.9	0.7	0.4		7489*)				
	6902	3.8	2.8	2.0	1.4		7552)				
	6910	1.3	0.9	0.7	0.4		7573)	2.6	1.9	1.5	1.1
² P° → ² P	7037	1.5	1.2	0.9	0.6	² D° → ² P					
	7128	0.9	0.7	0.5	0.3		7607)				
	7202	0.5	0.4	0.3	0.2		7755	4.8	3.5	2.7	2.0
							7800	2.7	2.1	1.6	1.1
^{*2} S° → ² P											

*²S° → ²P

Table (4.1)

Table (4.2) shows the measured appearance potentials, or thresholds for the emission line at 6856 Å, for all four target gasses. In addition, for each target, the thresholds for all the other emission lines were the same to within the accuracy of the measurement. Note that only a single threshold was measured per target, which indicates that only one dissociation mechanism is responsible for the 3p→ 3s emissions. Also shown in table (4.2) are the proposed dissociation channels along with the minimum energy required for each channel. Because of the large measured onsets, total fragmentation of the parent molecule is favored for all four target gases. The calculated energies are the energies required to form each parent molecule from its individual atomic constituents (heats of formation) and are taken from (Chase

Jr. *et al.*, 1985). In each case the measured threshold is 6 to 7 eV higher than the heat of formation which indicates an excess kinetic energy of approximately 1 eV per fragment which, in the case of SF_6 , is consistent with recent TOF data (Corr *et al.*, 1987).

Threshold energies for the emission at 6856 Å				
Target	Onset (eV)	Proposed dissociation channel	Calculated energy (eV)	ΔE (eV)
NF_3	29.7(± 1.5)	$\text{NF}_3 \rightarrow \text{N} + 2\text{F} + \text{F}^*(3\text{p})$	23.1	6.6
CCl_2F_2	37.0(± 2.0)	$\text{CCl}_2\text{F}_2 \rightarrow \text{C} + 2\text{Cl} + \text{F} + \text{F}^*(3\text{p})$	31.2	5.8
CF_4	41.0(± 1.5)	$\text{CF}_4 \rightarrow \text{C} + 3\text{F} + \text{F}^*(3\text{p})$	34.7	6.3
SF_6	41.6(± 1.5)	$\text{SF}_6 \rightarrow \text{S} + 5\text{F} + \text{F}^*(3\text{p})$	34.7	6.9

Table (4.2)

Fluorine $3s(^2\text{P}) \rightarrow 2\text{p}$ emissions from SF_6 , CF_4 , NF_3 and CCl_2F_2

In addition to spectra in the visible region, emission spectra in the VUV were taken for the four target gases SF_6 , CF_4 , NF_3 and CCl_2F_2 , and the corresponding emission cross sections were measured. Figure (4.4) shows the

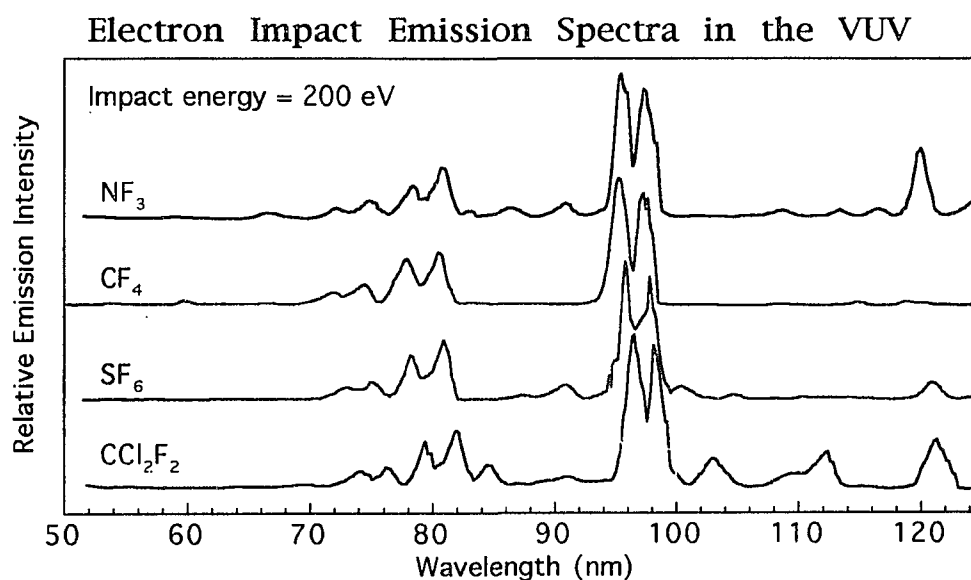


Figure (4.4)

emission spectra of all the target gases between 50 and 130 nm, taken at an impact energy of 200 eV. Common to all is the presence of the two atomic fluorine (FI) resonance $3s(^4,^2P) \rightarrow 2p(^2P^\circ)$ multiplets centered at 97.5 and 95.5 nm. Other features common to all are the emissions at 81 and 78 nm which are due to higher excited states of fluorine (FI). Differences occur above 100 nm, which in the case of NF_3 is due to the atomic nitrogen (NI) $3s(^4P) \rightarrow 2p(^4S^\circ)$ multiplet at 120 nm. Figure (4.5) shows the apparent emission cross sections for the integrated $3s(^2P) \rightarrow 2p(^2P^\circ)$ multiplet centered at 95.5 nm for the targets NF_3 , SF_6 and CF_4 . (Because of anomalies in the cross section, CCl_2F_2 will be discussed later.) Smooth curves have been drawn through the data points,

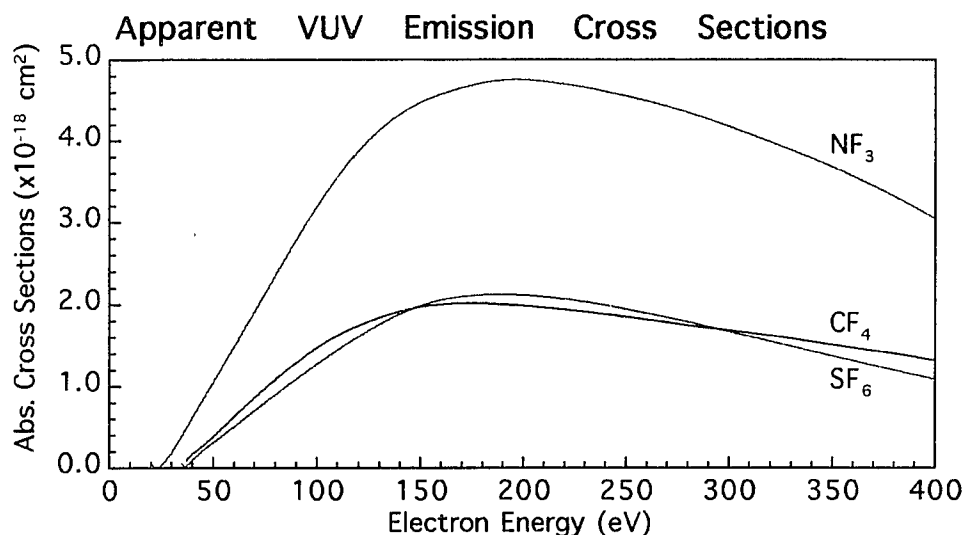


Figure (4.5)

which are not shown. The curves shown in figure (4.5) are the result of direct measurements and, as such, have an uncertainty of $\pm 20\%$ in the absolute value. However, as mentioned previously, $3p \rightarrow 3s(^2P)$ transitions contribute to the $3s(^2P) \rightarrow 2p$ emission cross sections through cascade. Figure (4.6) shows the emission cross sections with this contribution subtracted thereby giving the direct $3s(^2P) \rightarrow 2p(^2P^\circ)$ emission cross sections for the same target gases.

Figure (4.7) shows all three cross sections for the NF_3 target, indicating that the $3p \rightarrow 3s(^2P)$ cascade contribution is about 50% of the total, apparent cross section. The corresponding contribution to the SF_6 apparent cross section is 30%, and for CF_4 it is 75%. The advantage of using the measured $3p \rightarrow 3s(^2P)$

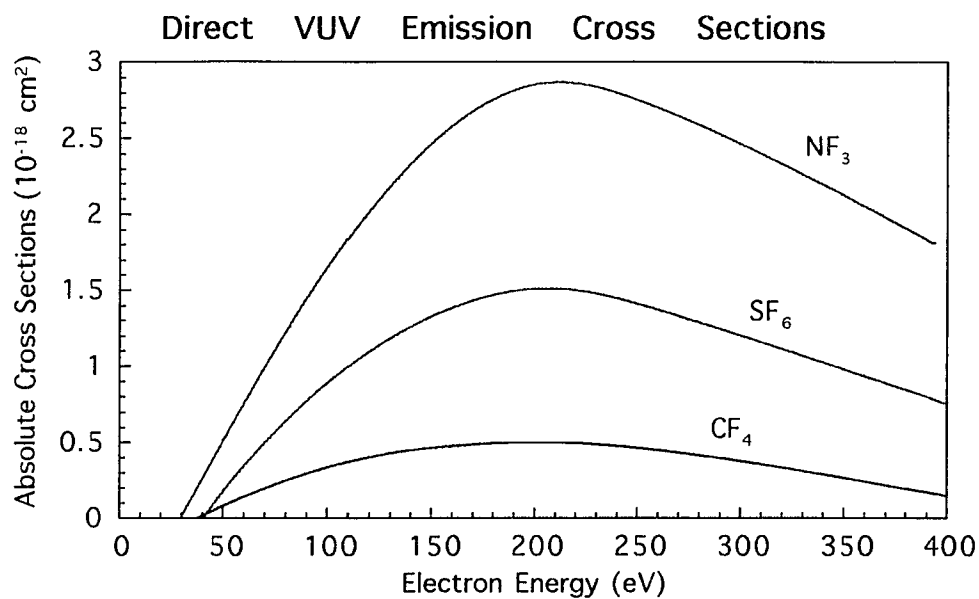


Figure (4.6)

emission cross sections over direct, dissociative excitation cross sections in

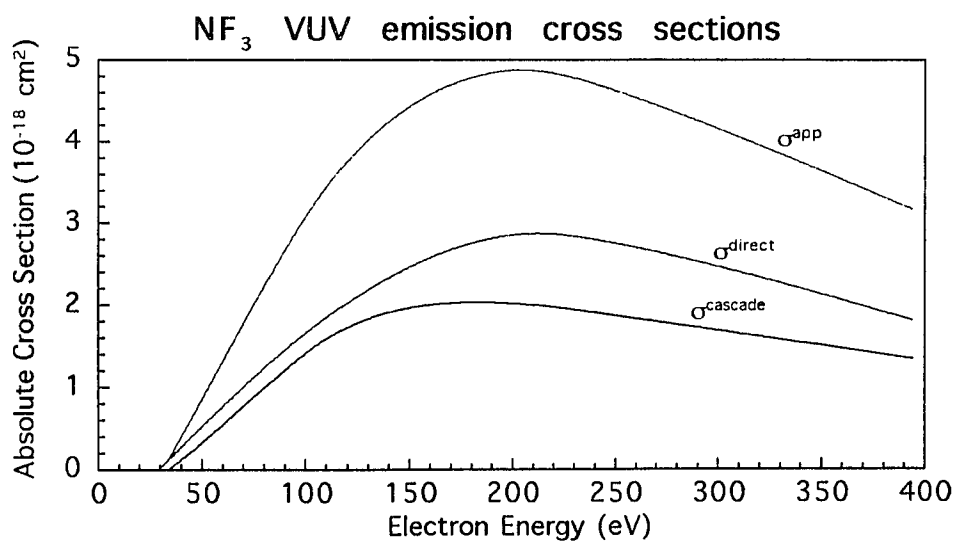


Figure (4.7)

determining the cascade contribution to the $3s(^2P) \rightarrow 2p$ emission cross sections is that the measured emission cross sections automatically include multiple cascades, with the only restriction being that the transition terminates in a $3p$ configuration. Cascading from other excited states, for example $nd \rightarrow 2p, n \geq 3$ has not been included, but is estimated to be small. If not, emissions from those states would be present in the measured VUV spectra. (In fact the observed emission features at 78 and 81 nm do contribute to the apparent emission cross section but are very small, as can be seen.) Since the $3s(^2P) \rightarrow 2p(^2P^\circ)$ transition is the only one possible for atoms in the $3s$ configuration, figure (4.6) represents the direct dissociative excitation cross sections to the $3s(^2P)$ state as well. Due to the added uncertainty from the $3p \rightarrow 3s(^2P)$ cascade contribution the uncertainty in the direct dissociative excitation cross sections increases to $\pm 30\%$.

Because of their importance in determining the dissociation mechanism, the minimum electron energies required for the $3s(^2P) \rightarrow 2p$ emissions were measured with great care. Table (4.3) summarizes these onsets for the targets NF_3 , SF_6 and CF_4 . All onsets were measured with an accuracy of ± 1.5 eV. As shown, two separate onsets were measured for each target which, as stated earlier, indicates two distinct dissociation channels leading to the same excited

FI $3s \rightarrow 2p$ Emission Threshold Energies				
Target	Onset 1(eV)	Minimum energy required for total fragmentation + $F^*(3s)$	Onset 2(eV)	Previously measured $3p \rightarrow 3s$ Onset
NF_3	24.9	21.7	29.7	29.7
CF_4	34.9	33.3	41.7	41.0
SF_6	36.1	33.3	41.5	41.6

Table (4.3)

state of the emitting fragment. In the present case, all of the second onsets are consistent with the previously measured FI $3p \rightarrow 3s(^2P)$ onsets, as shown in table (4.3). Therefore we make the reasonable assumption that, in the case of the targets NF_3 , SF_6 and CF_4 , the second thresholds represent the onset of the same dissociation channel leading to the production of excited fluorine atoms in the $3p$ configuration that was measured earlier, and that contributes to the apparent $3s(^2P) \rightarrow 2p$ emission cross section through $3p \rightarrow 3s(^2P)$ cascade. The measured first thresholds are compared to the same thermodynamic data (heats of formation) used earlier for the FI $3p \rightarrow 3s(^2P)$ emission cross sections (Chase Jr. *et al.*, 1985). As indicated in column three of table (4.3), all of the measured first onsets are 2 to 3 eV above the minimum energy required for the total fragmentation of the parent molecule into neutral ground state atoms plus an excited fluorine $\text{F}^* 3s(^2P)$ atom. We therefore attribute the first thresholds for FI $3s(^2P) \rightarrow 2p$ emissions to this dissociation channel (total fragmentation).

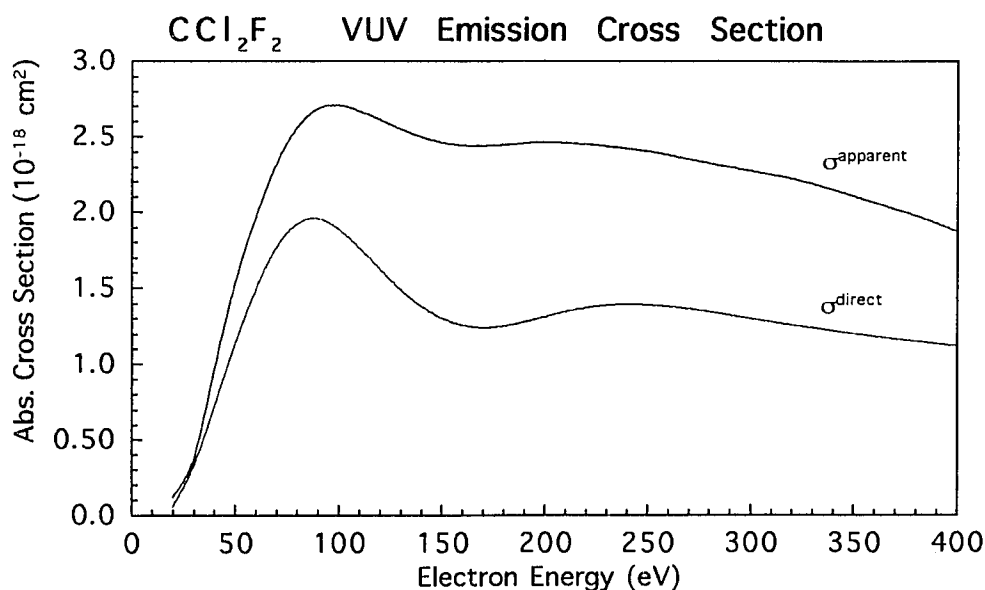


Figure (4.8)

Figure (4.8) shows the apparent and direct FI $3s(^2P) \rightarrow 2p$ emission cross sections for the CCl_2F_2 target gas. As with the other targets, the direct cross section is the apparent cross section with the FI $3p \rightarrow 3s(^2P)$ contribution subtracted. It is obvious from the figure that there are important differences between CCl_2F_2 and the other targets concerning the FI $3s(^2P) \rightarrow 2p$ emission cross section, which is the reason for a separate discussion. The two most striking differences are 1) $\sigma^{apparent}$ appears to have two relative maxima which is even more pronounced in σ^{direct} and 2) the first maximum in $\sigma^{apparent}$ and σ^{direct} occurs at a much lower electron energy (≈ 90 eV) compared with the other targets (175-210 eV). Another crucial difference concerns the emission threshold energies. As with the other targets, two distinct onsets were measured for the CCl_2F_2 FI $3s(^2P) \rightarrow 2p$ emissions. However, unlike the other targets, the first onset occurs at 21.0 eV which is less than the 29 eV required for total fragmentation. The second CCl_2F_2 onset occurs at 35.8 eV which, like the other targets, is consistent with the previously measured FI $3p \rightarrow 3s(^2P)$ onset of 37 ± 2 eV.

The interpretation of all these findings is as follows. Clearly the first onset results from a partial fragmentation of CCl_2F_2 . Table (4.4) lists the possible fragmentation channels and the energy required (Chase Jr. *et al.*, 1985). Because of the low measured emission threshold energy, the last two channels listed in table (4.4) are the most likely processes. Based on energy considerations alone it is impossible to determine which of these two is favored. However, since CCl_2 has been identified as a frequent product in the dissociation of chlorine containing molecules (Tokue *et al.*, 1990) we favor $CCl_2F_2 \rightarrow CCl_2 + F + F^*(3s^2P)$ as the most likely partial fragmentation channel leading to the production of excited fluorine $F^*(3s^2P)$ atoms. In addition, a possible dissociation channel is $CCl_2F_2 \rightarrow CCl_2F + F^*(3s^2P)$ although the stability

and heat of formation of the CCl_2F is unknown. Also, it seems reasonable to assume that the partial fragmentation channel responsible for the first onset

Possible CCl_2F_2 dissociation channels leading to the production of excited $\text{F}^*(3s^2\text{P})$ atoms	
Fragmentation products	Required Energy (eV)
$\text{C} + 2\text{Cl} + \text{F} + \text{F}^*(3s^2\text{P})$	29.0
$\text{C} + \text{Cl}_2 + \text{F} + \text{F}^*(3s^2\text{P})$	26.9
$\text{CCl} + \text{Cl} + \text{F} + \text{F}^*(3s^2\text{P})$	26.1
$\text{CF} + 2\text{Cl} + \text{F}^*(3s^2\text{P})$	24.0
$\text{CCl}_2 + \text{F} + \text{F}^*(3s^2\text{P})$	22.1
$\text{CF} + \text{Cl}_2 + \text{F}^*(3s^2\text{P})$	21.4

Table (4.4)

is also responsible for the first maximum in the $\text{FI } 3s(^2\text{P}) \rightarrow 2p$ apparent emission cross section. Concerning the second onset, since its location is consistent with the previously measured $\text{FI } 3p \rightarrow 3s(^2\text{P})$ onset, we interpret it as the opening of the same dissociation channel leading to the production of excited $\text{FI } 3p$ atoms that was measured earlier and which contributes to the apparent $3s(^2\text{P}) \rightarrow 2p$ emission cross section through $3p \rightarrow 3s(^2\text{P})$ cascade. This second dissociation channel may be responsible for the second apparent $3s(^2\text{P}) \rightarrow 2p$ emission cross section maximum seen in figure (4.8). However, the possibility of a third dissociation channel leading directly to the production of excited $3s(^2\text{P})$ fluorine atoms through the total fragmentation of the CCl_2F_2 parent molecule, in analogy with the other target molecules, cannot be discounted. It is possible that the expected onset associated with this third dissociation channel was present but was not detected.

Fluorine $3s(^4\text{P}) \rightarrow 2p$ emissions from SF_6 , CF_4 , NF_3 and CCl_2F_2

As mentioned, the other prominent feature in the VUV spectra of all four

target gases is the FI $3s(^4P) \rightarrow 2p$ multiplet centered at 97.5 nm. Apparent emission cross sections for this multiplet were measured for all four target gases which, in certain respects, were very similar to the corresponding $3s(^2P) \rightarrow 2p$ apparent emission cross sections. All corresponding $3s(^4P) \rightarrow 2p$ and $3s(^2P) \rightarrow 2p$ excitation functions had a similar overall shape and double onset structure. In fact, within our experimental uncertainty, all corresponding emission thresholds occurred at identical electron energies. However, our absolute $3s(^4P) \rightarrow 2p$ apparent emission cross sections results, based directly on intensity measurements, indicated that the apparent $3s(^4P) \rightarrow 2p$ cross sections were less than the $3p \rightarrow 3s(^4P)$ cross sections measured previously. Since we expect all $3p^4(S,P,D)^\circ$ fluorine atoms to undergo $3p \rightarrow 3s(^4P) \rightarrow 2p$ transitions, and therefore contribute to the apparent $3s(^4P) \rightarrow 2p$ emission cross section by cascade, our results suggest that $3s(^4P) \rightarrow 2p$ photons are being lost. It has been suggested, that because of the intercombinational nature of the $3s(^4P) \rightarrow 2p(^2P^\circ)$ multiplet, the lifetime of the $3s(^4P)$ state is long enough to allow an appreciable fraction of fluorine atoms to escape from the viewing region before decaying (Wang *et al.*, 1989) The same conclusion seems warranted in the present case. Table (4.5) illustrates the problem by showing

Absolute FI $3s(^4P) \rightarrow 2p(^2P)$ Emission Cross Sections (10^{-19} cm^2)

at 200 eV Electron Impact Energy

Target	$3s(^4P) \rightarrow 2p$ emission cross section (from intensity measurements)	$3p \rightarrow 3s(^4P)$ emission cross section (measured previously)	$3s(^4P) \rightarrow 2p$ emission cross section (from threshold analysis)
NF ₃	34.8	35.5	54.4
CF ₄	15.0	25.8	29.1
SF ₆	15.9	14.5	24.4
CCl ₂ F ₂	21.0	22.0	...

Table (4.5)

the intensity based $3s(^4P) \rightarrow 2p$ emission cross sections as well as the previously measured $3p \rightarrow 3s(^4P)$ cascade cross sections for all four target gases. In all cases the cascade cross section is larger than or comparable to the apparent cross section. Also shown are estimated apparent $3s(^4P) \rightarrow 2p$ emission cross sections that are based on a near threshold analysis, of the measured apparent cross sections. The following is a brief explanation of the procedure used, and figure (4.9) below gives an illustration. The linear portion of the measured excitation function just past the second threshold, attributed to the onset of the $3p \rightarrow 3s(^4P)$ cascade contribution is subtracted and, based on our previous measurements, the full $3p \rightarrow 3s(^4P)$ excitation function is extrapolated. From this we obtain, at any given electron energy, the ratio between the $3p \rightarrow 3s(^4P)$ emission cross section and the $3s(^4P) \rightarrow 2p$ apparent emission cross section.

Near Threshold Analysis Used to Estimate Apparent
 $(3s)^4P \rightarrow (2p)^2P^\circ$ Emission Cross Sections

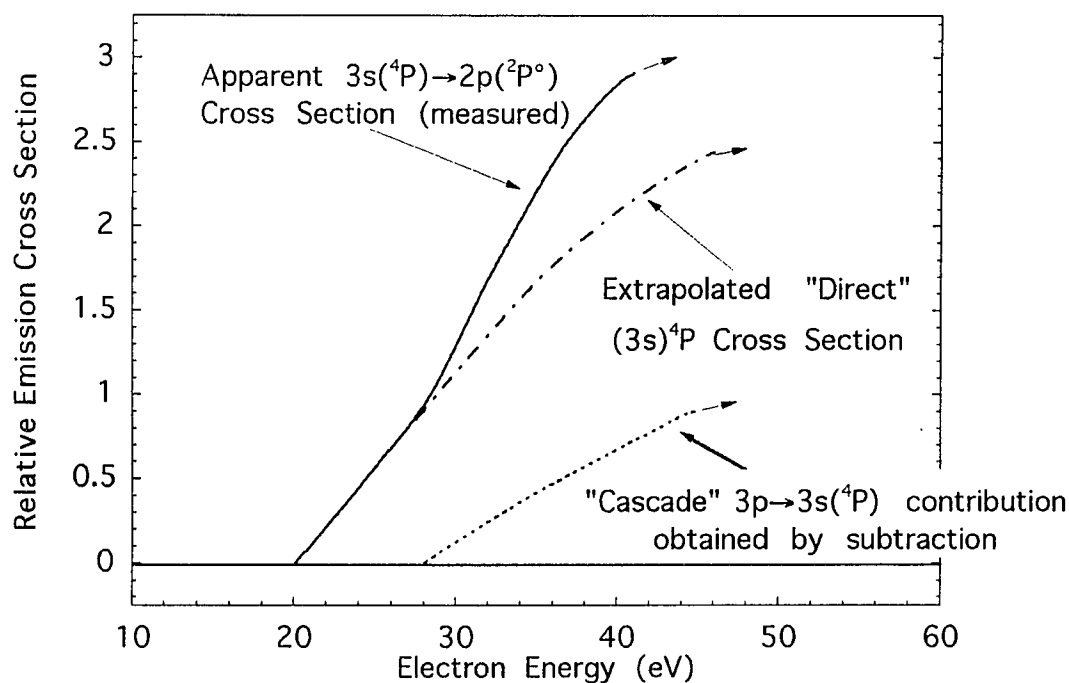


Figure (4.9)

Finally this ratio, based on our previous absolute $3p \rightarrow 3s(^4P)$ emission cross section measurements, is used to put the $3s(^4P) \rightarrow 2p$ apparent emission cross section on an absolute scale. The estimates obtained in this way are all larger than the corresponding $3s(^2P) \rightarrow 2p$ cross sections. Note that this procedure, based on the assumption of two well known and distinct dissociation channels, could not be carried out in the case of CCl_2F_2 .

Ultraviolet emissions (200-300 nm) from BCl_3

Shown in figure (4.10) is the ultraviolet spectrum produced by 200 eV electron impact on BCl_3 . The three most prominent features are the atomic boron lines at 208.9 and 249.7 nm corresponding to $2s2p^2(^2D) \rightarrow 2s^22p(^2P^\circ)$ and $2s^23s(^2S) \rightarrow 2s^22p(^2P^\circ)$ transitions, respectively and the BCl band system centered at 272.0 nm corresponding to the $A^1\Pi \rightarrow X^1\Sigma^+$ electronic transition. Note that the atomic boron (BI) "lines" are, in reality, unresolved doublets and that the BCl emission consists primarily of closely spaced vibrational bands, which correspond to the unresolved $\Delta v=0$ vibrational sequence.

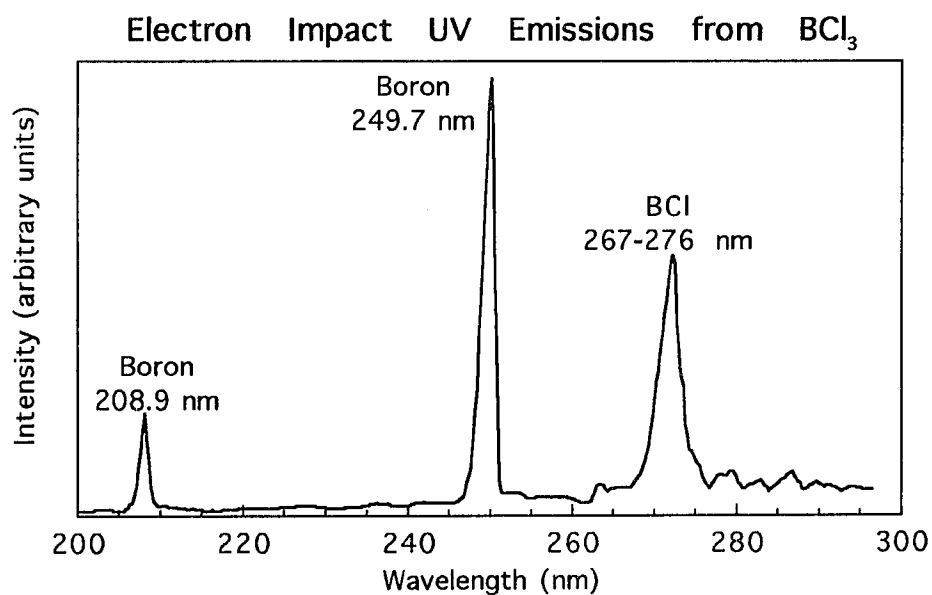


Figure (4.10)

Figure (4.11) shows the absolute electron-impact-produced emission cross sections of the boron line at 249.8 nm and the $\text{BCl } A^1\Pi \rightarrow X^1\Sigma^+$ vibrational band sequence between 267 and 276 nm from threshold to 100 eV impact energy. Two features are noteworthy. First, both emission cross sections, whose emissions are associated with mutually exclusive dissociation channels, show similar double onset structures such that the second onset is approximately 12 eV above the first. Although not shown, the emission cross section of the boron line at 208.9 nm also has a similar double onset structure. Second, both emission cross sections rise from threshold to a first maximum very quickly, within 6 eV in the case of the boron line. This rapid rise, unlike the much slower rise of the FI emission cross sections in the VUV from, e.g. NF_3 , suggests that the dissociative excited state of the BCl_3 parent molecule is reached by an optically forbidden transition (Miller Jr. *et al.*, 1987).

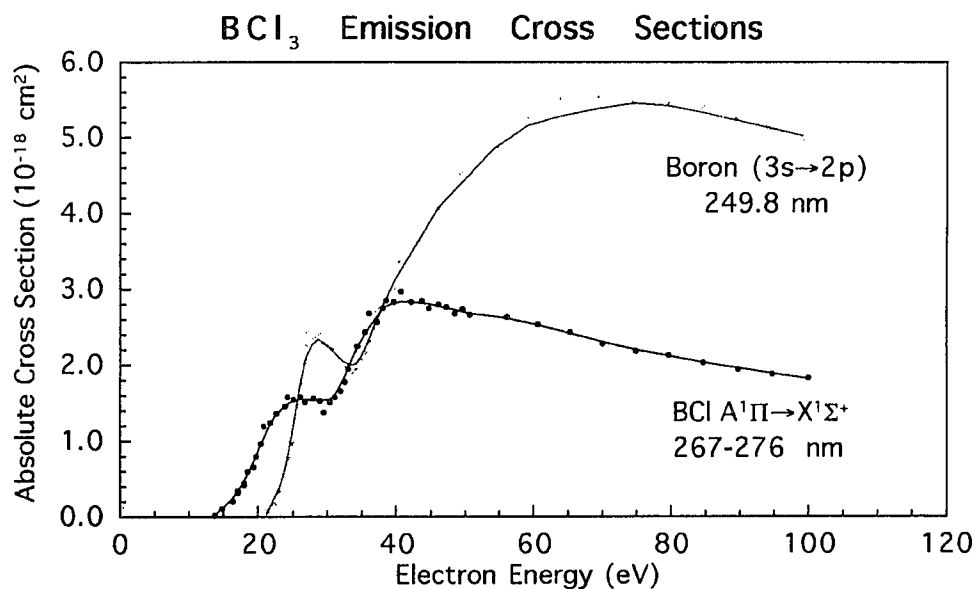
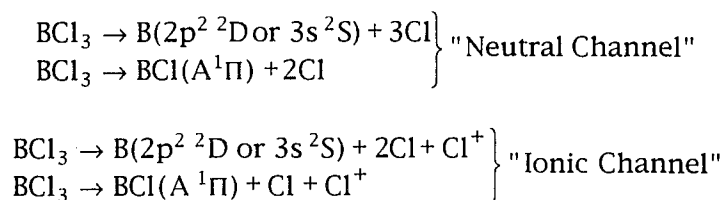


Figure (4.11)

Table (4.6) shows the measured onset energies for all three emission cross sections along with the heats of formation for two reaction pathways (Chase

Jr. *et al.*, 1985 and Radzig *et al.*, 1985), which are the dissociation channels whose thresholds are consistent with the measured onsets. Specifically, the dissociation of BCl_3 into an excited boron atom or boron chloride molecule and two or three ground state chlorine atoms, the "neutral channel", is the process with the largest threshold energy which is smaller than the measured onset for each emission. Also, because the 13.0 eV ionization potential of chlorine is consistent with the difference in measured



BCl ₃ Onsets and Dissociation Energies (eV)				
Emission	1 st Onset	Neutral Channel minimum energy	2 nd Onset	Ionic Channel minimum energy
B (208.9 nm)	23.0 (±1.5)	19.7	34.5(±2.0)	32.6
B (249.8 nm)	22.0(±1.5)	18.8	34.0(±2.0)	31.7
BCl (A→Σ ⁺)	14.0(±1.5)	13.1	29.0(±2.0)	26.0

Table (4.6)

onsets the same situation, with a ground state chlorine ion replacing a ground state chlorine atom applies to the "ionic channel". Therefore, we believe the neutral and ionic channels shown above are the most likely dissociation mechanisms leading to the observed emissions. Note that for both the atomic boron and the BCl emissions, neither second onset could be caused by the presence of a higher excited state in the emitting fragment, as was the case for the FI emissions in the VUV, because neither emitting fragment has a bound state in the range 13 eV above the excited state whose emissions are detected. (The ionization energy of boron and the dissociation energy of BCl are both

much smaller than 13 eV.)

In order to illustrate the roles of the different dissociation mechanisms, figure (4.12) shows the "neutral" and "ionic" channels of the $2s^23s(^2S) \rightarrow 2s^22p(^2P^\circ)$ boron line emission cross section at 249.8 nm separately. The high-energy part of the neutral channel was estimated by simply

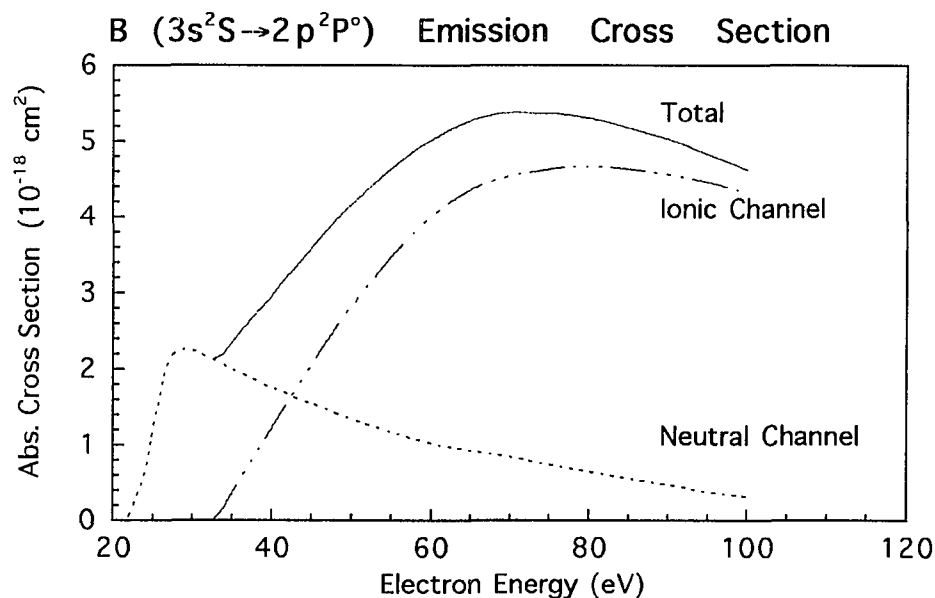


Figure (4.12)

extrapolating the low energy part to higher energies, and the ionic channel was constructed by subtracting the estimated neutral channel from the measured cross section, but the exact shapes are unimportant. The main feature of figure (4.12) is the slow rise to maximum of the ionic channel, which indicates that the excited state of the parent molecule is reached by an optically allowed transition, unlike the neutral channel. The same situation holds for the other boron line emission cross section ($2s2p^2(^2D) \rightarrow 2s^22p(^2P^\circ)$) at 208.9 nm as well as the $\text{BCl } A^1\Pi \rightarrow X^1\Sigma^+$ emission cross section.

Optical emissions between 2000 and 6000 Å from NF₃, CF₄, and SF₆

To complete the spectral survey, emissions from the targets NF₃, CF₄, and SF₆ in the range from 2000 to 6000 Å, between the previously discussed ranges of 75 to 130 nm in the VUV and 6000 to 8000 Å in the visible, were studied and will now be discussed briefly. (Optical detection between about 130 and 200 nm is problematic due to the low efficiencies of photon detectors in this range.)

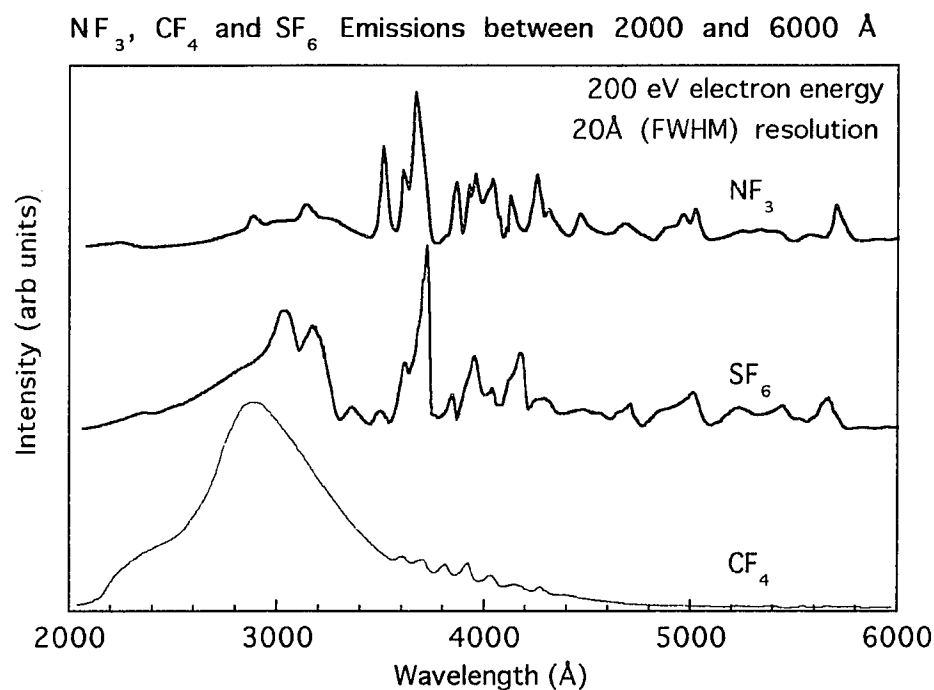


Figure (4.13)

Figure(4.13) above shows the emission spectra in this range produced by 200 eV electron impact on CF₄, SF₆, and NF₃ with a spectral resolution of 2 nm (Blanks *et al.*, 1987a). As can be seen, continuous as well as discrete emission features are present. Specifically, the CF₄ spectrum is dominated by a broad continuous emission feature, which extends from about 2000 to 5000 Å whereas both the SF₆ and NF₃ spectra consist of a continuous emission from about 2000 to 3200 Å as well as atomic fluorine (FI) line emissions corresponding to 4p → 3s transitions.

By far the most prominent feature of the three spectra shown above is the continuous emission from CF_4 , which extends from below 2000 Å to above 5000 Å. The integrated emission cross section for this feature is estimated to be $4.5(\pm 1.5) \times 10^{-17} \text{ cm}^2$ at 100 eV impact energy (Müller *et al.*, 1992), based on the measured value of $3.1(\pm 0.5) \times 10^{-17} \text{ cm}^2$ between 2600 and 5000 Å. This is to be compared with the most intense FI emission, due to the $\text{NF}_3 \text{ } ^2, ^4\text{D}^\circ \rightarrow \text{ } ^4\text{P}$ multiplet centered at 3668 Å which was measured to be $12.9(\pm 3.3) \times 10^{-20} \text{ cm}^2$ at the same energy (Blanks *et al.*, 1987a). The presence of the continuous CF_4 emissions have been known for at least 30 years. However, until recently, the emitting species had not been uniquely identified. Previous investigations of these emissions include radiative lifetime measurements using electron impact excitation (Hesser *et al.*, 1967), band cross section measurements following electron and ion bombardment (Aarts, 1985) and electron impact excited emission cross section measurements in the 50 to 130 nm wavelength range (Wang *et al.*, 1989). Additional experimental investigations of CF_4 include measuring the total dissociation cross section (Winters *et al.*, 1982), metastable fragment production (van der Burgt *et al.*, 1991), and the total and partial dissociative ionization cross sections (Ma *et al.*, 1991) as well as the double positive ion production (Bruce *et al.*, 1992). From energetic considerations, cross section shapes and comparisons with known CF and CF_2 emissions from electron impact excited CF_n ($n=1-4$) containing molecules, it is generally believed that the CF_4 continuous emissions originate from either CF_3^+ or CF_4^+ (Hesser *et al.*, 1967). Additionally, there has been some debate regarding the number of emitting species; *i.e.*, whether the emission consists of more than one fluorescence contribution. To answer these questions, investigations of the CF_4 continuous emissions were carried out simultaneously in our laboratory and the Universität des Saarlandes.

During the course of the investigations it was found that the presence of CF_4 in the vacuum chamber caused a large time dependent shift in the contact potential and therefore a time dependent error in the calibration of the electron beam impact energy which affected our earlier experiments with CF_4 , and perhaps a great many other experiments as well. In order to ensure an accurate electron energy scale, a rigorous *in situ* calibration procedure was used similar to the one employed for BCl_3 . With the use of this procedure the uncertainty in all onset energy measurements reported here is ± 2.0 eV, of which ± 1.2 eV can be attributed to the uncertainty in the electron impact energy calibration.

In order to determine the number of contributions to the observed fluorescence spectrum, optical excitation functions (relative photoemission cross sections) were measured every 5 nm from 225 to 400 nm with a resolution (FWHM) of 1.1 nm. Figure (4.14) below shows half of these excitation functions, spaced 10 nm apart. Two observations can be made concerning properties common to all of the excitation functions that are of crucial importance: 1.) all excitation functions had the same shape, with one broad maximum between 100 and 150 eV and 2.) within the ± 2.0 eV accuracy of the measurement, all excitation functions displayed the same onset of 23.5 eV. These results indicate that the CF_4 continuous emissions originate from a single emitting species, since presumably a second emitter would have a different fluorescence envelope and threshold energy. Additionally, every excitation function exhibited at about 40 eV a change in slope which became more apparent when higher statistical accuracy was used. We interpret this common feature as a second onset, or the opening of a second dissociation channel contributing to the CF_4 continuous emissions. Subsequently, wavelength scans were taken at impact energies below, at and above this

second onset by both laboratories with the result that no change in the fluorescence envelope was seen. This finding supports the notion that only a single radiating fragment is responsible for the observed emission from electron impact excited CF_4 , and that two channels contribute to this emission feature.

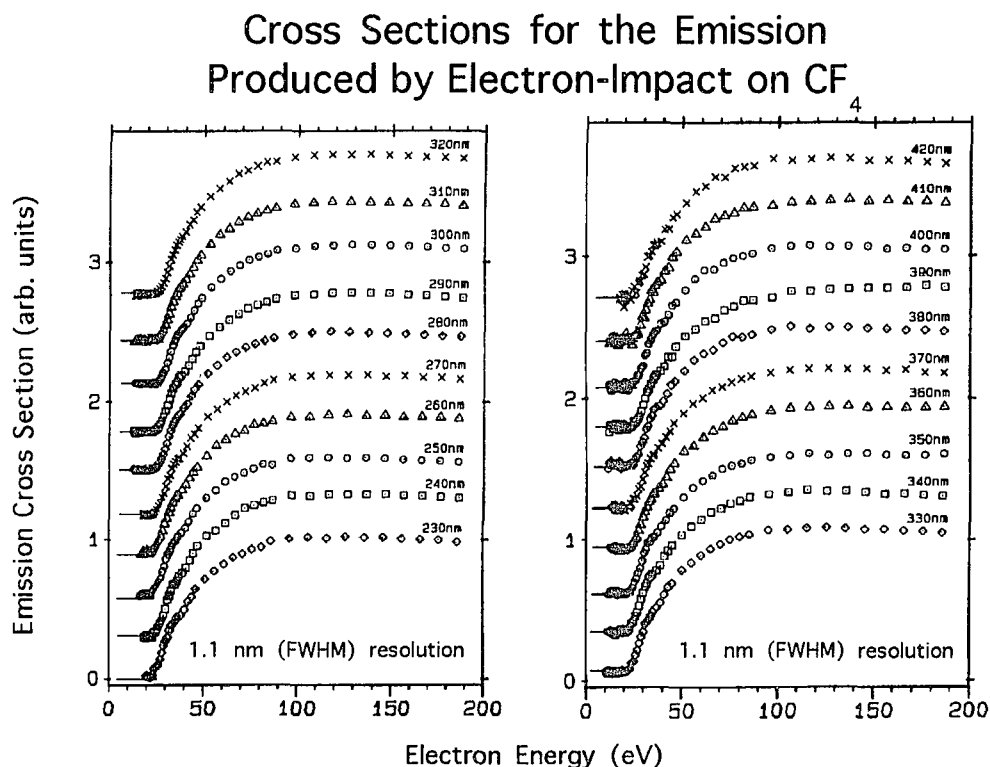


Figure (4.14)

We interpret the presence of a second onset as evidence that the observed CF_4 continuous emissions originate from excited $(\text{CF}_3^+)^*$ ions. Additionally, the evidence suggests that the excited $(\text{CF}_3^+)^*$ ions are produced by two dissociation channels, namely $\text{CF}_4 + e^- \rightarrow (\text{CF}_3^+)^* + \text{F} + 2e^-$ and $\text{CF}_4 + e^- \rightarrow (\text{CF}_3^+)^* + \text{F}^+ + 3e^-$ with thermodynamically determined minimum energies (Chase Jr. *et al.*, 1985) of 19.5 and 36.9 eV, respectively. This conclusion is similar to that found from the electron impact induced UV spectrum of BCl_3 , the only difference being that

the resulting molecular emissions came from a known electronic transition of BCl.

The SF₆ and NF₃ spectra each consist of a continuous emission feature between about 2000 and 3200 Å and several FI emission lines due to 4p→3s transitions. As can be seen, for both SF₆ and NF₃ the most prominent FI emission is the ^{2,4}D°→⁴P multiplet centered at 3668 Å. The photoemission cross sections for this multiplet were measured to be $(4.4 \pm 1.2) \times 10^{-20}$ and $(12.9 \pm 3.3) \times 10^{-20}$ cm² for SF₆ and NF₃, respectively, at an impact energy of 100 eV. In the case of SF₆, a single onset of 40(±2) eV was found which is consistent with the previously found 3p→3s emission onsets. Furthermore, the shape of the 4p→3s cross section was found to be similar to the previously measured 3p→3s cross section shapes. This indicates that the same dissociation channel, namely, total fragmentation of the parent SF₆ molecule, is dominant in both cases, and the same conclusion is found for NF₃. In addition, some additional lines can be seen in the NF₃ spectrum which are not present in the SF₆ spectrum. These are due to the singly charged fluorine ion, F(II), and have very high onsets (100 to 110 eV).

Lastly, a separate investigation of the SF₆ and NF₃ continuous emissions ranging from 2000 to 3200 Å was conducted by (Jabbour *et al.*, 1988a). The results will only be summarized briefly for completeness. In the case of NF₃, the emissions were found to consist of two components, a structured feature with peaks at 2880, 3005, and 3130 Å, and a continuum. The structured emission had an onset of 8.5 ± 2 eV and was attributed to excited NF₂ fragments, whereas the continuum displayed an onset of 30 ± 3 eV whose origin could not be uniquely determined. It is interesting to note that very recent calculations of the dissociative excitation of NF₃ using the complex Kohn method produced a cross section shape very similar to what we measured for the unstructured NF₂

emission (Rescigno, 1995). In the case of SF_6 , the emissions were again found to consist of two components, a broad emission with a peak at 3010 Å and a narrower weak emission centered at 3160 Å. The broad emission was found to have two onsets at $28(\pm 2)$ and $42(\pm 3)$ eV, whereas the narrower emission had only a single onset at $13.5(\pm 1.5)$ eV. For both emission components these onsets are high enough to allow a large number of partial fragmentation channels to be responsible. Therefore, spectroscopic and energetic considerations alone are insufficient to determine the source of the continuous emissions between 2000 and 3200 Å in the case of SF_6 .

Part II. The Triple Beam Experiment

V. Introduction

The previous sections described our experiments involving the detection of excited state atomic or molecular fragments produced by the electron impact induced dissociation of simple halogen containing molecules. The dissociation fragments were detected by the radiation they emitted upon decay. The spectrum of emitted radiation indicated what excited state fragments were produced, and the intensities of particular identifying emission features indicated the probability with which they were produced. When the effects of cascade from higher excited states and branching to lower excited states are taken into account, the resulting excitation functions (intensities of emission features versus electron impact energy) are related to the probability with which the target molecule dissociates into a particular excited state of the emitting fragment. When emission spectra are measured covering the entire range in which electronically excited atoms and simple molecules typically radiate (from the VUV to the infrared), it becomes possible to measure the probability with which the target molecule dissociates into *all* excited states of the emitting fragment. However, in order to assess the importance of a particular dissociation channel to the dissociation of the parent molecule, the production of ground state fragments must also be taken into account. In fact, since dissociation into ground state fragments is expected to be much more probable than dissociation into excited state fragments, their detection and measurement is crucial to the study of electron impact dissociation.

Therefore, as an extension of our ongoing investigation into the electron impact dissociation of simple halogen containing molecules and for the purpose of measuring the probability of neutral ground state fragment

production following electron impact, a new apparatus was designed, built and experiments were begun. In addition to gas and electron beam sources similar in principle to those employed in the old apparatus (referred to as the "photoemission experiment"), the new apparatus utilizes a tunable pulsed dye laser system. Since three beams are employed, (gas, electron, and laser beams) the new apparatus will be referred to as the "**triple beam**" experiment.

Because neutral atoms and molecules in their ground states possess neither excess energy nor charge, they are "impossible" to detect without resorting to chemical processes; *i.e.*, adsorption, the application of which depends strongly on the particular species being detected. In contrast, the triple beam experiment has been designed to detect virtually any ground state atomic or molecular fragment resulting from any electron impact phenomenon. In the triple beam experiment, a laser is used to transfer energy to a selected ground state species. This energy is in the form of a resonantly absorbed photon which is subsequently re-emitted. The presence of the ground state atom or molecule is revealed when a fraction of the re-emitted photons, in a direction other than the laser beam, is detected. Because every atom or molecule has a different set of resonant frequencies and the laser has a sufficiently narrow bandwidth, unique identification of the absorbing species is possible. This technique, known as laser induced fluorescence (LIF), consists of using the laser as a probe to measure the presence of neutral ground state fragments which result from an electron impact process.

In order to measure the probability for the production of neutral ground state products resulting from electron impact dissociation we use the fact that the intensity of the LIF signal is proportional to the rate with which ground state fragments are produced. In addition, it must be remembered that radiation associated with the decay of excited state products is also present and

the intensity of the signal from this radiation, to be called the "excited state signal" is proportional to the rate of their production. Therefore, the ratio of the LIF signal to the "excited state signal" is proportional to the ratio of probabilities for producing ground state and excited state fragments, respectively. If the probability, or cross section for the production of excited state fragments is known the cross section for the production of ground state fragments can be deduced. The details of how this ratio is measured are given in the following sections.

VI. Operating Principles and Theoretical Background

The triple beam experiment was designed to measure cross sections for the production of ground state species produced by electron impact dissociation using laser-induced fluorescence (LIF). However, the LIF technique is more general than that; essentially any species that can be optically pumped to a bound excited state can be detected. Therefore, to demonstrate the feasibility of the proposed technique, we were able to select a process that does not involve dissociation for the first set of experiments. The process chosen was the electron impact ionization of N_2 , specifically $N_2(X^1\Sigma_g^+) + e^- \rightarrow N_2^+(X^2\Sigma_g^+) + 2e^-$. We are able to study this reaction because the final product, $N_2^+(X^2\Sigma_g^+)$ can be detected by LIF and it can be distinguished from all other ground state electron impact products such as N_2 , N , and N^+ by its unique absorption spectrum, which is well known (Lofthus *et al.*, 1977). Additionally, we chose to study this reaction because its cross section is already known, or can be deduced from published data (Itikawa *et al.*, 1986), so that our (re)measurement serves to check the method and to calibrate our apparatus.

Rotational Structure of the $N_2^+(B^2\Sigma_u^+ \leftrightarrow X^2\Sigma_g^+)$ Band System

In one part of the present experiment N_2^+ in its $X^2\Sigma_g^+$ ground state is raised to its $B^2\Sigma_u^+$ excited state by the absorption of laser light and the subsequent fluorescence is monitored as a function of laser wavelength (LIF). Specifically, the laser is tuned to pump the $X^2\Sigma_g^+ \rightarrow B^2\Sigma_u^+$ ($v'=0, v''=0$) band, and the resulting absorption is measured by monitoring the subsequent $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ ($v'=0, v''=1$) spontaneous emission, as shown in figure (6.1) below. Since the bandwidth of the laser is less than the spacing between individual rotational lines, we obtain a rotationally resolved absorption spectrum of $N_2^+(X^2\Sigma_g^+)$. The present discussion focuses on the rotational structure, or J dependence (J

labels the total angular momentum of the molecule, neglecting nuclear spin) of the N_2^+ ($B^2\Sigma_u^+ \leftrightarrow X^2\Sigma_g^+$) band system. Topics concerning how properties of the incident radiation, *i.e.*, the polarization and the power, affect the observed absorption spectrum will be dealt with subsequently.

N_2^+ Energy Levels for LIF

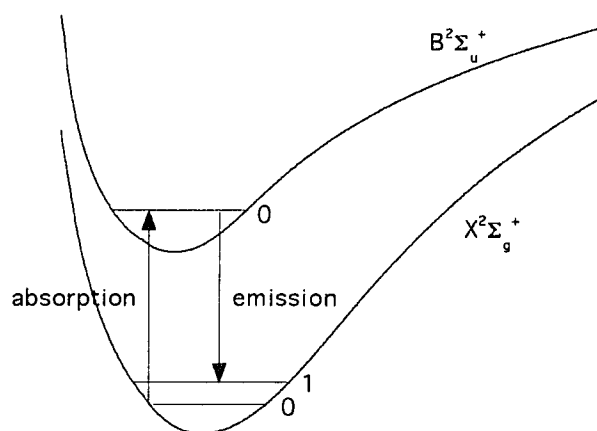


Figure (6.1)

Since the symmetry of the total molecular eigenfunction is independent of the vibrational quantum number, v , each (v', v'') band within a band system possesses the same rotational structure. Therefore all conclusions of the present section apply to every (v', v'') band of the N_2^+ ($B^2\Sigma_u^+ \leftrightarrow X^2\Sigma_g^+$) band system (Herzberg, 1950).

As an example of a $^2\Sigma \leftrightarrow ^2\Sigma$ electronic transition, the N_2^+ ($B^2\Sigma_u^+ \leftrightarrow X^2\Sigma_g^+$) band system is accurately described by Hund's coupling case (b) (Herzberg, 1950). Except for the splitting due to the coupling of the electronic spin with the rotational motion of the molecule, known as ρ -doubling, and the intensity alternation of successive lines of the rotationally resolved spectrum (rotational lines) due to the extra symmetry of the eigenfunctions of homonuclear diatomic molecules, the rotational structure of the

N_2^+ ($B^2\Sigma_u^+ \leftrightarrow X^2\Sigma_g^+$) band system is the simplest possible for a transition involving two electronic states of a diatomic molecule.

The expression for the relative intensity of the rotational lines of the $X^2\Sigma_g^+ \rightarrow B^2\Sigma_u^+$ ($v'=0, v''=0$) band is given as (Demtröder, 1981 and Herzberg, 1950)

$$I(BJ', XJ'') = S_{J'', \Delta J}^{^2\Sigma \leftrightarrow ^2\Sigma} e^{-E_{J''}/kT} \quad (6.1)$$

where $I(BJ', XJ'')$ is the relative intensity of the $J'' \rightarrow J'$ rotational line, $S_{J'', \Delta J}^{^2\Sigma \leftrightarrow ^2\Sigma}$ is the part of the line strength that depends on J , and $E_{J''}$ is the rotational energy of the, initial, J'' level. Note that all factors independent of J'' and J' have been suppressed. Also note that all factors in equation (6.1) above pertain to the absorbing transition (because all the emitted light of the (0,1) band is detected the J dependence of the emission line strength disappears). The rotational energy, $E_{J''}$ is given by $B_v'' J''(J''+1)$, where B_v'' is the rotational term constant of the $X^2\Sigma_g^+ v''=0$ ground state (Herzberg, 1950). As shown below, line strengths and selection rules appropriate for $^1\Sigma \leftrightarrow ^1\Sigma$ transitions can be used in the present case. Therefore, each band of the $B^2\Sigma_u^+ \leftrightarrow X^2\Sigma_g^+$ band system consists of a P branch ($\Delta J=-1$) and an R branch ($\Delta J=+1$), with $S_{J'', -1}^{^1\Sigma \leftrightarrow ^1\Sigma} = J''$ and $S_{J'', +1}^{^1\Sigma \leftrightarrow ^1\Sigma} = J'' + 1$. The expression $e^{-E_{J''}/kT}$ is the Boltzmann factor representing the probability of finding an N_2^+ molecule in the J'' level. Because all target gases used in the present experiment can be considered in equilibrium at room temperature (295 °K), there is a negligible probability of finding a molecule in other than its ground electronic and vibrational states. However, because the magnitude of the rotational energy is comparable to the thermal energy at room temperature (0.0254 eV), rotational levels other than $J=0$ are appreciably populated. Specifically, for $N_2^+(X^2\Sigma_g^+)$, $v=0$ the $J=7$ level has the greatest population. It has been discovered (Allison *et al.*, 1979, DeKoven *et al.*, 1981, Helvajian *et al.*, 1984, Nagata *et al.*, 1987, and Zetner *et al.*, 1988) that the

effective rotational temperature of $N_2^+(X^2\Sigma_g^+)$ and $N_2^+(B^2\Sigma_u^+)$ ions produced by electron impact in a supersonic jet increases as the energy of the electron beam decreases. In a supersonic jet the internal degrees of freedom are "cooled" at the expense of directed translational motion, so that rotational temperatures of only a few Kelvin can be achieved (Helvajian *et al.*, 1984, Nagata *et al.*, 1987, and Zetner *et al.*, 1988). This lower rotational temperature manifests itself in an increased population of the lower J'' levels, as would be expected from the Boltzmann factor. Since the observed warming is small and since in the present experiment room temperature N_2 is used, the rotational temperature is effectively constant; *i.e.*, independent of the electron beam energy, and a value of 295 °K will be used throughout.

The ρ -doubling causes a splitting of the R and P branch lines, which are single for a $^1\Sigma \leftrightarrow ^1\Sigma$ transition, into two components. In addition there is a satellite Q branch, but its intensity decreases quickly with increasing N , making it very difficult to observe. (In Hund's case (b), N is the quantum number corresponding to the angular momentum from the rotation of the nuclei about the center of mass of the molecule coupled to the orbital angular momentum of the electrons about a line joining the two nuclei. Since, in the present case, we are dealing exclusively with Σ states, the electronic orbital angular momentum is zero and N is referred to as the "rotational" quantum number.) The ρ -doubling increases linearly with N and has been measured to be approximately 0.3 cm^{-1} ($0.04 \text{ \AA}$) for $N''=24$ in the P branch (Bouchoux *et al.*, 1976). Since the bandwidth of the laser is approximately 0.2 cm^{-1} and the intensity of the R and P branch lines is greatest for $N''=7$ (see above) it is very unlikely that the ρ -doubling will be observed in the present experiment. Therefore, the rotational structure of the $N_2^+(B^2\Sigma_u^+ \leftrightarrow X^2\Sigma_g^+)$ spectrum can be treated as a $^1\Sigma \leftrightarrow ^1\Sigma$ transition; *i.e.*, single R and P branch lines and no Q

branch. Specifically, Hönl-London factors (the J dependent part of the line strength) appropriate for $^1\Sigma \leftrightarrow ^1\Sigma$ transitions can be used, multiplied by a factor of 2 for the unaccounted spin degeneracy, instead of the Hönl-London factors used for $^2\Sigma \leftrightarrow ^2\Sigma$ transitions.

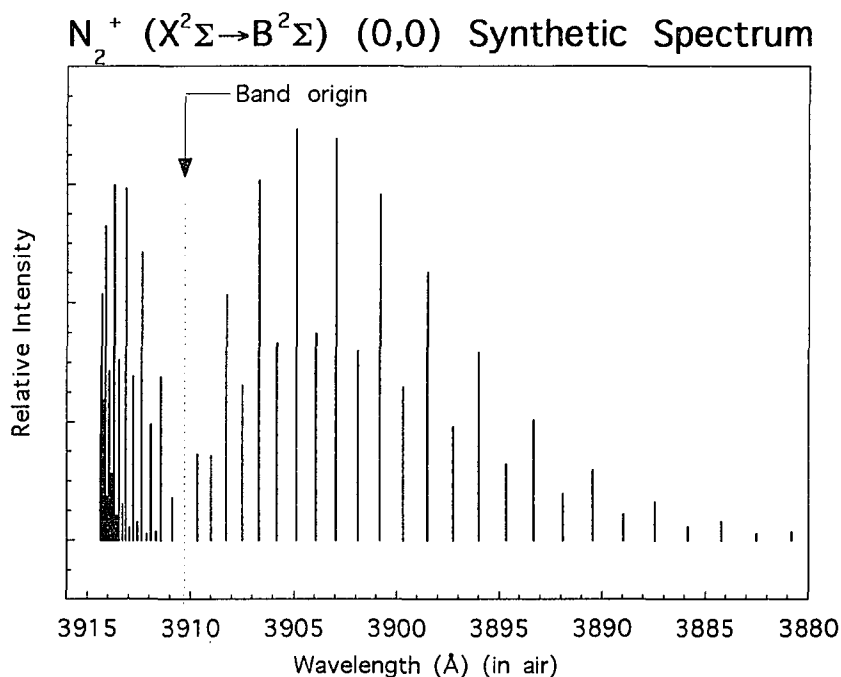


Figure (6.2)

The intensity alternation of successive lines of the rotationally resolved spectrum mentioned above is a phenomenon affecting only homonuclear molecules, such as $^{14}\text{N}_2^+$. It is a result of the symmetry of the molecule under the exchange of its nuclei, the subsequent symmetry property of the eigenfunctions, and the resulting selection rule based on this symmetry property. All eigenfunctions of a homonuclear diatomic molecule are either symmetric or anti-symmetric with respect to an exchange of the individual nuclei. This results in the general (and very powerful) selection rule that prohibits symmetric levels from combining with anti symmetric levels under any kind of interaction (Herzberg, 1950).. (Note that, for homonuclear

diatomic molecules whose nuclei have a non-zero spin, interactions that depend on the orientation of the spin of the nuclei **can**, in fact, connect symmetric and anti-symmetric levels. However, typically these interactions do so only very slowly.) Intensity alternation of successive lines of the rotational spectrum then follows from the fact that these lines originate alternately from symmetric and anti symmetric levels, and that for homonuclear diatomic molecules symmetric and anti symmetric levels carry different statistical weights. In the case of $^{14}\text{N}_2^+$ (and $^{14}\text{N}_2$) the result is 2:1 symmetric to anti-symmetric ratio. For the $^2\Sigma$ ground state of $^{14}\text{N}_2^+$, levels with N even are symmetric, N odd anti-symmetric (both ρ -doubling components have the same symmetry), which results in the 2:1 observed intensity ratio of even to odd levels. Figure (6.2) above shows a synthetic, $\text{N}_2^+(X^2\Sigma_g^+ \rightarrow B^2\Sigma_u^+)$ (0,0) band, excitation spectrum which takes the rotational temperature, ρ -doubling, and intensity alternation, just discussed, into account.

The Electronic Structure and Ionization Mechanisms of N_2

The configuration of the $X^1\Sigma_g^+$ ground state of N_2 and the $X^2\Sigma_g^+$ ground state and $B^2\Sigma_u^+$ excited state of N_2^+ are given as

$$\text{N}_2(X^1\Sigma_g^+) (\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^4(\sigma_g 2p)^2$$

$$\text{N}_2^+(X^2\Sigma_g^+) (\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^4(\sigma_g 2p)$$

$$\text{N}_2^+(B^2\Sigma_u^+) (\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s) (\pi_u 2p)^4(\sigma_g 2p)^2$$

in the separated atom approximation (Lofthus *et al.*, 1977). It is seen that the $\text{N}_2^+(X^2\Sigma_g^+)$ ground state results from the removal of a $\sigma_g 2p$ outer valence electron and the $\text{N}_2^+(B^2\Sigma_u^+)$ excited state results from the removal of a $\sigma_u 2s$ inner valence electron from the ground state configuration of N_2 (Fons *et al.*, 1994). In addition, it is seen that $\text{N}_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$ emission is due to the

$\sigma_g 2p \rightarrow \sigma_u 2s$ one electron transition.

There is a difference between the ionization mechanisms leading to $N_2^+(X^2\Sigma_g^+)$ and $N_2^+(B^2\Sigma_u^+)$ which is now discussed. $N_2^+(B^2\Sigma_u^+)$ is created via electron impact through a purely dipole interaction; *i.e.*, the final Σ_u^+ state is obtained from the initial Σ_g^+ state through a dipole allowed transition. This is not the case for the production of $N_2^+(X^2\Sigma_g^+)$, since the final state is a Σ_g^+ , and Σ_g^+ states do not combine with other Σ_g^+ states in the dipole approximation (Herzberg, 1950). Another way to see this is the following. $\Sigma_g^+ \leftrightarrow \Sigma_g^+$ dipole transitions, with $\Delta J = \pm 1$ would violate the rigorous symmetric $\leftrightarrow$ anti symmetric selection rule, discussed in the preceding section, which holds for homonuclear diatomic molecules. However, there is contrary evidence that points to the production of $N_2^+(X^2\Sigma_g^+)$ through interactions that are dipole in character. This evidence comes from partial photoionization experiments in which the cross section for the production of the various final states of the ion can be determined (Brion *et al.*, 1981). These experiments reveal that $N_2^+(X^2\Sigma_g^+)$ results with a probability as large as or larger than $N_2^+(B^2\Sigma_u^+)$. Additional evidence comes from an examination of the estimated $N_2(X^1\Sigma_g^+) + e^- \rightarrow N_2^+(X^2\Sigma_g^+) + 2e^-$ cross section at high incident electron energies. Specifically, a Fano plot of the estimated cross section reveals a positive slope of the straight line asymptote, which indicates that dipole allowed mechanisms dominate the ionization process. As an explanation of this phenomenon, it has been suggested by (Zetner *et al.*, 1988) that production of $N_2^+(X^2\Sigma_g^+)$ proceeds through an excited complex that consists of a $^1\Sigma_u^+$ or $^1\Pi_u$ ionic core plus ejected electron which rapidly autoionizes to the final $^2\Sigma_g^+$ state of the N_2^+ ion. In this model, the ejected electron carries away the odd parity necessary to give the overall $\Sigma_g^+ \leftrightarrow \Sigma_g^+$ transition a dipole character. It has been further suggested by (Zetner *et al.*, 1988) that the $^1\Sigma_u^+$ or $^1\Pi_u$ ionic core results from an extension

into the continuum of two observed Rydberg series, the Worley-Jenkins Rydberg series and the Carroll-Yoshino Rydberg series (Lofthus *et al.*, 1977). Observation of the angular distribution of ejected electrons coincident with $N_2^+(X^2\Sigma_g^+)$ production could verify this hypothesis. However, such an experiment has not yet been done.

Estimate of the $N_2(X^1\Sigma_g^+) + e^- \rightarrow N_2^+(X^2\Sigma_g^+) + 2e^-$ ionization cross section

The cross section for the production of N_2^+ ions in their $X^2\Sigma_g^+$ ground state by electron impact on N_2 in its $X^1\Sigma_g^+$ ground state can be estimated from previously measured cross sections. Specifically, $\sigma[N_2^+(X^2\Sigma_g^+)] = \sigma[N_2^+(\text{total})] - \sum \sigma[N_2^+(\text{exc. states})]$, where $\sigma[N_2^+(\text{total})]$ and $\sigma[N_2^+(\text{exc. state})]$ are the cross sections for the production of N_2^+ ions into all final states and into a specific excited state, respectively.

The measurement of $\sigma[N_2^+(\text{total})]$ is relatively straightforward, requiring only a mass analysis of the resultant ions, the major experimental difficulty being the determination of the ion collection efficiency as a function of ion kinetic energy. For $\sigma[N_2^+(\text{total})]$ the recent data of (Krishnakumar *et al.*, 1990) are taken. On the other hand, the estimate of $\sigma[N_2^+(\text{exc. state})]$ is more problematic, because it is determined from emission cross sections. Typically, emission cross sections for electronic excited states of a molecule are given as band emission cross sections. They are obtained by measuring the excitation function for a particular (v', v'') band or a group of (v', v'') bands, where v' is the vibrational quantum number of the upper state and v'' the vibrational quantum number of the lower state. For emission cross sections in the visible and UV, there is always a change in the electronic quantum number, often only implied, and labeled with lower or upper case letters. Following the procedure of (Aarts *et al.*, 1971), the cross section for (v', v'') emissions,

$\sigma(v', v'')$, is related to the vibrational excitation cross section, $\sigma(v' \rightarrow v'')$ by

$$\sigma(v') = \sum_{v''} \sigma(v', v'') = \sigma(v' \rightarrow v'') \frac{\sum_{v''} A_{v', v''}}{A_{v', v''}}, \quad (6.2)$$

where the sum is over all lower vibrational states v'' , the $A_{v', v''}$'s are the spontaneous transition probabilities (Einstein A coefficients) for the $v' \rightarrow v''$ transition, and the last equality is simply an example of the use of the molecular branching ratio. Finally, the cross section for the production of the excited state, $\sigma(n')$, where n labels the electronic state is related to $\sigma(n', v')$ by

$$\sigma(n') = \sum_{v'} \sigma(n', v') = \sigma(n', v') \frac{\sum_{v'} I_{v'}}{I_{v'}}, \quad (6.3)$$

where $\sum_{v'} I_{v'}/I_{v'}$ is the relative probability for exciting the level v' of the state n' . The factor $\sum_{v'} I_{v'}/I_{v'}$ can be obtained from measurements or, as is the case here, estimated from Franck-Condon factors for ionization (Märk, 1984).

Only two excited states of N_2^+ are produced with appreciable cross sections; namely, the $A^2\Pi_u$ state and the $B^2\Sigma_u^+$ state. Higher excited states of N_2^+ exist, for example the $C^2\Sigma_u^+$ and $D^2\Pi_g$ states, but since emissions from their band systems are very weak, it is estimated that they do not contribute significantly to the total N_2^+ production (Fons *et al.*, 1994). Combining equations (6.2) and (6.3) above and using $A_{v', v''}$ coefficients and ionization Franck-Condon factors from Lofthus *et al.*, (1977), estimates for the production of $N_2^+(A^2\Pi_u)$ and $N_2^+(B^2\Sigma_u^+)$ are obtained. The results are $\sigma[N_2^+(A^2\Pi_u)] = 4.07 \sigma[N_2^+; A \rightarrow X; (1,0)]$ and $\sigma[N_2^+(B^2\Sigma_u^+)] = 1.64 \sigma[N_2^+; B \rightarrow X; (0,0)]$, where the quantities on the left are excitation cross sections and the quantities on the right are emission cross sections and emission cross sections from (Piper *et al.*, 1986 and Borst *et al.*, 1970) were used to obtain the above results. The cross section for the production of ground state N_2^+ ions is then obtained by simply performing the

subtraction mentioned above; *i.e.*, $\sigma[N_2^+(X^2\Sigma_g^+)] = \sigma[N_2^+(\text{total})] - \sigma[N_2^+(A^2\Pi_u)] - \sigma[N_2^+(B^2\Sigma_u^+)]$. The result is shown in figure (6.3) below.

It should be noted that in estimating the cross sections for exciting a particular electronic excited state (excitation cross section), the effects of cascade from higher excited states were not included. In fact, $D^2\Pi_g \rightarrow A^2\Pi_u$ emissions have been detected and their emission cross sections have been measured (Fons *et al.*, 1994). However, their intensity suggests that the $D^2\Pi_g \rightarrow A^2\Pi_u$ cascade contribution to $A^2\Pi_u \rightarrow X^2\Sigma_g$ is only about 1%. In the same experiment, $D^2\Pi_g \rightarrow B^2\Sigma_u$ emissions were sought, but no discernible signal was found. Therefore, cascade from the $D^2\Pi_g$ state is not expected to appreciably affect the estimate of $N_2^+(X^2\Sigma_g^+)$ production. On the other hand, excitation cross

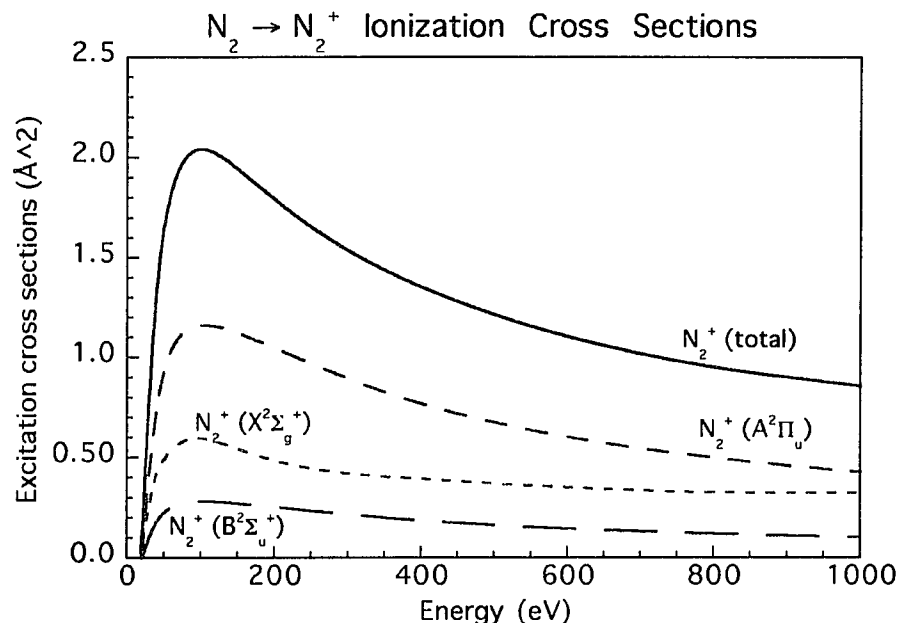


Figure (6.3)

section estimates are only as accurate as the emission cross sections on which they are based. Borst and Zipf's $B^2\Sigma_u \rightarrow X^2\Sigma_g(0,0)$ emission cross section (Borst *et al.*, 1970) has long been regarded as the standard for that emission, and it has often been used as a secondary standard to which other, relative cross

section measurements have been normalized. On the other hand, there have been variations of about a factor of two among various $A^2\Pi_u \rightarrow X^2\Sigma_g$ emission cross section measurements. This is most likely caused by collisional quenching due to the relatively long ($\approx 10\mu s$) $A^2\Pi_u(v)$ lifetime. (Piper *et al.*, 1986) estimated the ratio of the cross section for $A^2\Pi_u$ state production to that of $B^2\Sigma_u$ state production to be 4.1 ± 0.7 . This can be checked by noting that at high incident energies electron impact ionization can be related to photoionization through the use of the Bethe-Born approximation. The Bethe-Born approximation states that the integrated electron impact ionization cross section, in the limit of high impact energy, is given by the expression $\sigma = AE^{-1} \ln(BE)$ (Inokuti, 1971 and Märk, 1984), where E is the energy of the incident electron and A and B are constants for a given atom or molecule. The constant A equals $\int_{E_i}^{\infty} \left(\frac{df}{dE}\right) \frac{Ry}{E} dE$ where df/dE is the optical oscillator strength density, Ry is the Rydberg energy (13.606 eV), and E_i is the ionization potential. The constant A is, in fact, the continuum contribution to the $S(-1)$ moment of the oscillator strength distribution and is simply related to the photoionization cross section through the expression $S(-1) \propto \int_0^{\lambda_{IP}} \frac{\sigma_{\gamma}(\lambda)}{\lambda} d\lambda$ (Berkowitz, 1979), where $\sigma_{\gamma}(\lambda)$ is the photo ionization cross section and λ_{IP} is the wavelength corresponding to the ionization potential. The comparison of electron-impact ionization and photo ionization data is facilitated by the use of a Fano plot in which σE is plotted versus $\ln(E)$. At high energies the resulting curve approaches a straight line whose slope is A . Therefore, the estimate of the ratio of the $N_2^+(A^2\Pi_u)$ to $N_2^+(B^2\Sigma_u^+)$ excitation cross sections can be tested by comparing the ratio of the slopes of their Fano plots with the ratio of $S(-1)$ values obtained from photoionization experiments. Using data compiled by (Berkowitz, 1979) a ratio of 5.4 is obtained for $S_{A^2\Pi}(-1)/S_{B^2\Sigma}(-1)$. This compares reasonably well with Piper's estimate of $4.1(\pm 0.7)$ and certainly indicates that

the earlier $N_2^+(A^2\Pi_u)$ excitation cross section measurements were too low.

Laser Induced Fluorescence

Laser induced fluorescence (LIF), of an isolated atom or molecule in its ground state consists of the absorption of a photon, provided by the laser, and the subsequent re-emission of a photon whose energy, direction, and polarization are different from that of the incident photon. LIF, an example of resonance fluorescence, is distinguished from a light scattering process such as Rayleigh scattering by the following properties. With resonance fluorescence, the photon absorption raises the atom or molecule to a real, not a virtual, excited state, and the energy of the absorbed photon equals the difference in energy between the excited and ground states. Actually, there is a narrow range of photon energies that can be absorbed, usually governed by the uncertainty in measuring the energy of the excited state, which gives the resonance a finite width. The subsequent decay of the excited state, accompanied by the emission of a photon (fluorescence), takes place after a time that is characteristic of the excited state, called the lifetime. In contrast, a light scattering process is non-resonant and takes place on a time scale several orders of magnitude shorter than resonance fluorescence.

For the purposes of detecting the presence of a ground state atom or molecule, the utility of LIF comes from exactly those properties that distinguish it from light scattering; namely, resonant absorption of a photon and the subsequent re-emission of a photon with known properties on a known time scale. In the current experiment, LIF is used to measure the population of N_2^+ in its $X^2\Sigma_g^+$ ground state. Specifically, $N_2^+(X^2\Sigma_g^+)$ ($v_i=0, J_i$) ions are pumped by the laser to the $B^2\Sigma_u^+$ ($v_e=0, J_e=J_i\pm 1$) excited state, a known fraction subsequently decays back to the $X^2\Sigma_g^+$ ($v_f=1, J_f=J_e\pm 1$) ground state, and

a portion of the $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+ (0,1)$ radiation emitted at right angles to the laser beam is detected. The relationship between the measured LIF signal and the $N_2^+(X^2\Sigma_g^+) (v=0, J)$ population consists of two parts. The first part depends on intrinsic properties of the N_2^+ ion such as the absorption probability of the $N_2^+(X^2\Sigma_g^+) (v=0, J)$ ground state and the spontaneous emission probability of the $B^2\Sigma_u^+ (v=0, J)$ excited state. The second part depends on the interaction of the incident radiation with the ensemble of target N_2^+ ions. Specifically, the measured LIF signal depends in a nontrivial manner on the intensity and polarization of the incident laser beam, and the distribution of angular momentum vectors of the N_2^+ ions in their $X^2\Sigma_g^+$ ground states. This dependence has often been overlooked, but in order to make an accurate measurement of the $N_2^+(X^2\Sigma_g^+) (v=0, J)$ population its determination is essential.

Basic Formulation and its Limitations

The equation relating the LIF signal to the incident laser power is given by

$$I(\mathbf{a}, \mathbf{b}, \mathbf{c}) = K N_a A(\mathbf{b}, \mathbf{c}) B(\mathbf{a}, \mathbf{b}) \rho(v_i) \tau \quad (6.4)$$

(Kinsey, 1977). Here $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ are sets of quantum numbers labeling the initial, intermediate, and final states, and the only restriction is that the energy of state $\mathbf{b}$ must be higher than those of states $\mathbf{a}$ and $\mathbf{c}$. The quantity $I(\mathbf{a}, \mathbf{b}, \mathbf{c})$ is the instantaneous rate of fluorescence, integrated over all directions and two independent polarizations; $\rho(v_i)$ is the radiation density (mW/Hz-cm^3) of the incident laser beam at the resonant frequency of the $\mathbf{a} \rightarrow \mathbf{b}$ transition ($\rho(v_i)$ is assumed to be constant over the width of the resonance); N_a is the number of molecules in the initial (ground) state intersected by the laser beam; $B(\mathbf{a}, \mathbf{b})\rho(v_i)$ is the transition rate or probability per unit time that a molecule in the initial (ground) state $\mathbf{a}$ absorbs a photon from the incident laser beam and makes a transition to the intermediate

(excited) state **b**; $A(\mathbf{b},\mathbf{c})$ is the spontaneous emission rate or probability per unit time that a molecule in state **b** spontaneously decays to final state **c**; τ is the lifetime of excited state **b**; and K is a constant that depends on the detector and experimental geometry. The factors $A(\mathbf{b},\mathbf{c})$ and $B(\mathbf{a},\mathbf{b})$, known as the Einstein A and B coefficients are, apart from numerical factors, the squares of the dipole transition matrix elements connecting the two states involved in the particular transition ($\mathbf{a} \rightarrow \mathbf{b}$ or $\mathbf{b} \rightarrow \mathbf{c}$). All necessary A and B coefficients regarding the $B^2\Sigma_u^+ \leftrightarrow X^2\Sigma_g^+$ transitions in N_2^+ have been measured or calculated previously (Lofthus *et al.*, 1977).

Equation (6.4) is valid in the regime where the incident laser does not significantly alter the population of atoms or molecules in the initial state **a**, and where the target atoms or molecules are exposed to the incident radiation for a time much longer than the lifetime of the intermediate state **b**. However, in the present experiment we use laser pulses whose duration is much shorter than the intermediate state lifetime, so that there is no spontaneous decay of the "optically pumped" state **b** during the laser pulse. Additionally, we only collect fluorescence once the laser pulse has terminated. Therefore, equation (6.4) must be modified to include these conditions, and the relation between the laser induced fluorescence intensity and the incident radiation becomes

$$I(\mathbf{a}, \mathbf{b}, \mathbf{c}) = K N_a A(\mathbf{b}, \mathbf{c}) B(\mathbf{a}, \mathbf{b}) \rho(\nu_i) \Delta t_L e^{-t/\tau}, \quad (6.5)$$

where Δt_L is the duration of the laser pulse, which is assumed to be a rectangular function of time, and t is measured from the end of the laser pulse. The factor $N_a B(\mathbf{a}, \mathbf{b}) \rho(\nu_i) \Delta t_L$ in equation (6.5) above gives the number of atoms or molecules in excited state **b** at the end of the laser pulse. If all of the fluorescence is collected; *i.e.*, equation (6.5) is integrated with respect to time beginning with the end of the laser pulse, the factor $e^{-t/\tau}$ is replaced by τ , and

the factor $\tau_A(\mathbf{a}, \mathbf{b})$, which results, gives the probability that an atom or molecule in excited state $\mathbf{b}$ spontaneously decays to final state $\mathbf{c}$. $\tau_A(\mathbf{a}, \mathbf{b})$ is known as the branching ratio of the $\mathbf{b} \leftrightarrow \mathbf{c}$ transition. Therefore, when all of the fluorescence is collected, equation (6.5) represents the joint probability that an atom or molecule initially in state $\mathbf{a}$ absorbs a photon from the laser and is promoted to state $\mathbf{b}$, then subsequently decays to state $\mathbf{c}$, emitting a fluorescent photon. Implicit in the Einstein coefficients used in equation (6.5) is an average over an isotropic distribution of orientations of the transition dipole involved in the $\mathbf{a} \leftrightarrow \mathbf{b}$ transition and two independent polarizations of the incident laser beam, as well as the sum over all directions and two independent polarizations of the emitted radiation.

Equation (6.5) is correct but is not useful in a real experimental setup, including the current one, because it is impossible to detect the fluorescence in all directions, which, as just stated, was implicit in its derivation. In addition, most lasers used in LIF experiments are linearly polarized and the polarization axis is rarely changed when measurements are being made, so that the average over two independent polarizations of the laser is not made. Also, the assumption of equal magnetic substate populations of the initial state may not hold. (Even if it does hold, it is useful to have a theory that allows for this possibility, because the populations of atoms or molecules in the different possible magnetic substates of the initial state depend sensitively on how the initial state was prepared, and therefore their measurement is a sensitive test of models of reaction dynamics (Fano *et al.*, 1973 and Greene *et al.*, 1983). In the current experimental configuration, where the incident electron beam is unpolarized and the scattered electrons are not detected, equal magnetic substate populations lead to a value of zero for the polarization of the fluorescence (Fano *et al.*, 1973). Based on the result that the polarization of

$B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ radiation from $N_2^+(B^2\Sigma_u^+)$ molecules created via electron impact of N_2 is zero (Borst *et al.*, 1970), we expect the assumption of equal magnetic substate populations in the initial ($X^2\Sigma_g^+$) state to hold. However, equation (6.5) still has to be modified to account for the detection of fluorescence over a finite solid angle and the fixed polarization of the laser. The fixed polarization of the laser leads to polarized fluorescence, even under the condition of equal magnetic substate populations (isotropic distribution of angular momentum vectors). The polarization of the fluorescence is important, even when it is not measured, because it is intimately connected with the anisotropy of the emitted radiation (see equation (2.7)). The anisotropy of the radiation, in turn, results in a variation of the measured fluorescence intensity at different angles of detection.

Lastly, equations (6.4 and 6.5) are valid only when the fluorescence intensity varies linearly with the laser power. The range of incident radiation densities, or laser powers where this holds is known as the unsaturated regime. As the laser power is increased beyond this regime, the phenomenon of saturation becomes important. The onset of the saturated regime occurs when the LIF intensity begins to increase less than linearly with the laser power, and the transition is said to be fully saturated when the LIF intensity is totally independent of the laser power. (Eventually, the signal may even decrease). Additionally, the degree of polarization, and therefore anisotropy of the fluorescence, varies with the incident laser power, which further alters the relationship between the initial state population and the observed LIF intensity. Clearly the theory leading to equation (6.5) must be expanded to include polarization and saturation effects. Since different analyses are required, the cases of the unsaturated and saturated regime are treated separately below.

Polarization and Anisotropy in the Unsaturated Regime ($B(a,b)\rho(v_i)\Delta t_L \ll 1$)

The polarization of laser induced fluorescence results from the dependence of the electric dipole transition matrix element on the orientation of the angular momentum vector of an atom or molecule in the initial state **a**. Specifically, for linearly polarized light, the absorption probability is proportional to $(\hat{\epsilon} \cdot \bar{\mu})^2$, where $\hat{\epsilon}$ is the polarization axis of the laser and $\bar{\mu}$ is the transition dipole moment of the **a** → **b** transition ($\bar{\mu} = -e\langle a|\vec{r}|b\rangle$). Next, the direction of $\bar{\mu}$ has a fixed relationship to the orientation of the angular momentum vector $\vec{J}$, which depends on the magnitude J of the initial state **a**, as well as the ΔJ involved in the **a** → **b** transition (Case *et al.*, 1978). Therefore, the absorption probability of an atom or molecule in initial state **a** depends on the orientation of its angular momentum vector with respect to the polarization axis of the laser. For an isotropic distribution of **a** state angular momentum vectors, table (6.1) below gives the polarization of the laser induced fluorescence for the four possible combinations of absorbing ($R\uparrow$ and $P\uparrow$) and emitting ($R\downarrow$ and $P\downarrow$) branches which accompany the $X^2\Sigma_g^+ \leftrightarrow B^2\Sigma_u^+$ electronic transitions that are pumped and monitored in the current experiment (Feofilov, 1961). The polarizations shown in table (6.1) arise solely from the anisotropy of the resonance fluorescence process itself. The limiting value of the polarization for large J is $1/7$ in all cases. In the present experiment, the polarization of the emitted radiation is not measured and the

Transition	Polarization
$P\uparrow P\downarrow$	$\frac{(J-1)(2J-3)}{14J^2+5J+1}$
$P\uparrow R\downarrow$	$\frac{1}{7}$
$R\uparrow R\downarrow$	$\frac{(J+2)(2J+5)}{14J^2+23J+10}$
$R\uparrow P\downarrow$	$\frac{1}{7}$

Table (6.1)

$R\downarrow$ and $P\downarrow$ transitions are not resolved. Therefore, the observed intensity corresponds to the sum of two perpendicular directions of the polarization analyzer and both downward transitions. Figure (6.4) below shows the variation of the observed intensity as a function of J due to the variation of the polarization. (The variation of the intensity due to the thermal distribution of J values, shown in figure (6.2) is not included.) The observed intensity is shown for two different experimental configurations: observation parallel and perpendicular to the polarization axis of the laser (Greene *et al.*, 1983). As shown, the variation is small for large J , but is large for $J \leq 2$. In experiments involving supersonic beams, where small rotational temperatures result in large initial populations with $J \leq 2$, failure to account for this variation can lead to serious errors when extracting populations from LIF measurements.

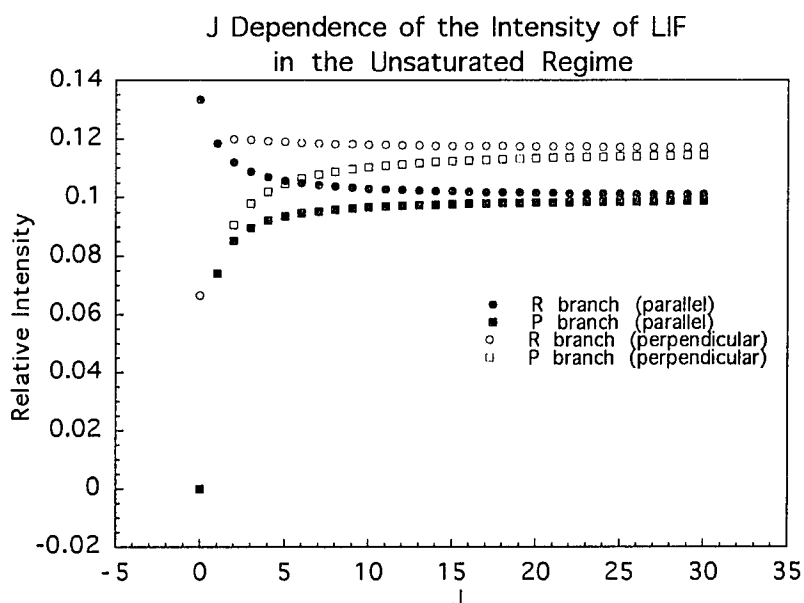


Figure (6.4)

Saturated Regime ($B(a,b)p(v_i)\Delta t_L \gg 1$)

Equations (6.4 and 6.5) do not predict the upper limit of the LIF intensity that is readily observed when pulsed lasers with pulse energies of a few

hundred μJ , pulse durations of a few ns, and bandwidths less than a few tenths of an $\text{\AA}$ are used. The upper limit that occurs is caused by stimulated emission that puts an upper bound on the number of atoms or molecules left in the intermediate state **b** at the end of the laser pulse. When this limit is reached, the ensemble of atoms or molecules becomes transparent to the laser light, and the amount of observed fluorescence becomes independent of the laser power. This implies that pulse to pulse fluctuations in laser pulse energies have no effect on the population of the upper state of the pumped transition. In addition, as the laser power is increased and all orientations of the angular momentum of the initial state are pumped sufficiently "hard" to cause saturation, the anisotropy of the absorption disappears, and the polarization of the fluorescence vanishes. This implies, for an isotropic distribution of angular momentum vectors in the initial state, that when the absorbing transition is fully saturated, the observed LIF intensity is independent of the direction of observation and the polarization axis of the laser beam. These features of saturation are extremely desirable when extracting initial state populations from LIF intensity measurements. In addition to being useful, it may be necessary to saturate the absorbing transition just to observe an LIF signal, because the population of atoms or molecules in the initial state may be small.

The upper limit of the population of the upper state **b** at the end of the laser pulse is given by $N_a \frac{g_b}{g_a + g_b}$, where g_a and g_b are the statistical weights (degeneracies) of the lower and upper levels being pumped. Therefore, when the $\mathbf{a} \leftrightarrow \mathbf{b}$ transition is strongly saturated, equation (6.5) becomes

$$I(\mathbf{a}, \mathbf{b}, \mathbf{c}) = K N_a \left(\frac{g_b}{g_a + g_b} \right) A(\mathbf{b}, \mathbf{c}) e^{-t/\tau} \quad (6.6)$$

In the present experiment, g_a equals $2J_i + 1$, and g_b equals $2J_e + 1$, where J_i and

J_e are the angular momentum quantum numbers of the initial (ground) and final (excited) states of the $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ (0,0) transition being pumped by the laser. It should be noted that this analysis has been used previously. Using a flowing afterglow source and a "mild" jet expansion to inject $N_2^+(X^2\Sigma_g^+)(v)$ ions into a flow tube Kato *et al.*, (1993) recently claimed to have reached a level of saturation where equation (6.6) applies and analyzed their data accordingly. Also, using a set of rate equations and directional Einstein coefficients (Einstein coefficients that have not been averaged over isotropic distributions of absorbed or emitted light and two independent polarizations) to model the LIF process, Altkorn *et al.*, (1984) have shown, for an isotropic distribution of angular momentum vectors in the initial state and transitions involving only R and P branches, that the polarization of the fluorescence becomes negligible and the fluorescence intensity reaches its saturated limit when the absorption probability, $B(a,b)\rho(v_i)\Delta t_L$, reaches a value of approximately 100. In the present experiment, values of the absorption probability much greater than this were routinely attained. We therefore expect to use equation (6.6) to extract $N_2^+(X^2\Sigma_g^+)$ populations from our measured LIF intensities.

Lastly, according to the strong field theory developed by Rabi (Demtröder, 1981), the transition probability induced by a strong field incident on an atom or molecule is time dependent. In addition, the time dependence is periodic (Demtröder, 1981). Therefore, in the unfortunate circumstance that the incident laser power and pulse duration coincide with the period of a Rabi oscillation, the ensemble of atoms or molecules is left in exactly the same condition as before the beginning of the laser pulse; *i.e.*, the fluorescence intensity is zero! This phenomenon limits the laser power that can be used to achieve the maximum change in the population of the lower state involved in an optical pumping process. A simple calculation shows that for the present

experiment, using $100 \mu \text{ J/laser pulse}$ which is more than sufficient to achieve the strong saturation limit, $\Delta t_L/T$ is only about 10^{-4} where T is the period of a Rabi oscillation. Therefore, Rabi oscillations will not decrease the maximum population change in the saturated limit, given by equation (6.6).

VII. Design and Operation of the Apparatus

A new experimental setup was designed and built to be used for the triple beam experiment. Since the triple beam experiment, discussed here, is an extension of the photoemission experiment, previously described, it can be expected that there are many similarities between the apparatus. On the other hand, the addition of the laser system necessitated numerous novel design features. In addition, all parts of the new apparatus were designed specifically to accommodate the special needs of the triple beam experiment. These modifications and design considerations are discussed in the following paragraphs.

Figure (7.1) below gives a schematic diagram of the major components of the triple-beam apparatus. Only those components outside the vacuum chamber are shown. These include the laser system and associated optics, the vacuum system, and the radiation detection system. Though technically not an

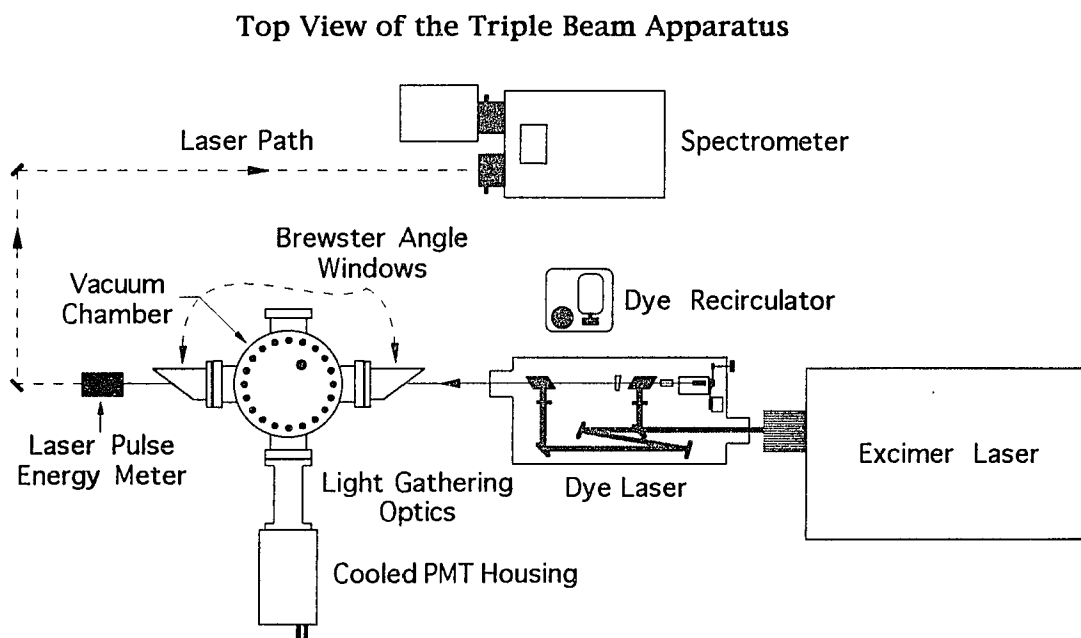


Figure (7.1)

integral part of the apparatus, the optical spectrometer used to measure the wavelength and linewidth of the laser is also shown. Shown separately in figure (7.2) below are the major components inside the vacuum chamber. These include the gas nozzle, the electron monochromator, the Faraday cup, and the primary lens used to collect the emitted light. Each system is now discussed separately.

Triple Beam Apparatus from inside the Vacuum Chamber

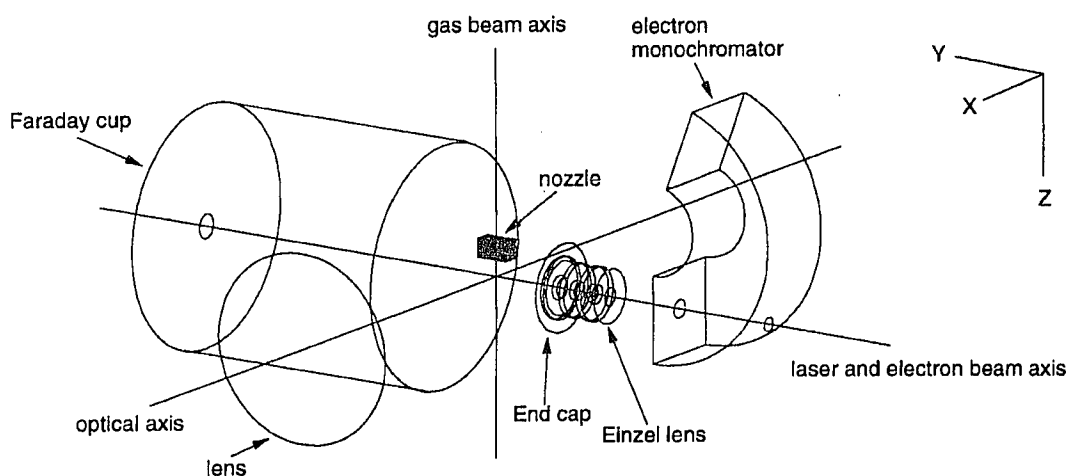


Figure (7.2)

The Vacuum and Gas Delivery Systems

The triple-beam apparatus is housed in a cylindrical vacuum chamber approximately 18" tall and 6" in diameter. Attached to the vacuum chamber are four ports in a horizontal plane, 90° apart, that are used as the entrance and exit ports for the laser beam, and the exit port for the emitted radiation. There is also an additional port that is used for the ionization gauge. The gas beam nozzle, electron monochromator, and Faraday cup shown in figure (7.2) are mounted on a circular stage that is attached to the top flange of the vacuum chamber by a vertical shaft and bellows assembly. The height of the

stage can be varied by expanding or contracting the bellows. The vacuum chamber is made of stainless steel and has flanges compatible with copper gaskets for ultra-high vacuum (UHV) use. Since UHV pressures are not required in the present experiment, Viton o-rings are used to seal the ports that are opened frequently and copper gaskets are used to seal the other ports.

We used a Balzers model TSH 332 pumping station which consists of a turbomolecular pump backed by a rotary vane mechanical pump. A turbo pump was chosen to ensure an oil free vacuum chamber; model TSH 332 was chosen because it can handle corrosive gases. The outlet of the pumping system is connected to a sealed exhaust line that terminates at the closed laboratory exhaust hood. A pressure slightly below atmospheric pressure is maintained inside the exhaust hood. The pumping station achieves a nominal pumping speed of 300 l/sec which results in a base pressure, without target gas, of approximately 2×10^{-7} torr. The injection of gas is controlled by a leak valve, (Granville Phillips model 203) and monitored with a capacitance manometer (MKS model 122AA). With a pushing pressure (pressure behind the nozzle) of 0.5 torr the operating pressure inside the vacuum chamber is approximately 2×10^{-5} torr.

The Laser System

As shown in figure (7.1), the laser system consists of an excimer laser (Lumonics Ex-520), which is used to pump a dye laser (Lumonics EPD-330). The Xe, Cl₂, He, and Ne gas required for the Ex-520 were obtained from Spectra Gases in the quantities and purities specified by Lumonics. During the course of the experiment two different dyes were used in the dye laser, Rhodamine 590 and Exalite 392A, both purchased from Exciton. The Rhodamine is used for laser output around 590 nm, the Exalite around 390 nm. The Rhodamine 590

was used for preliminary work such as initial alignment and wavelength calibration, while Excalite 392A was used for the LIF studies of N_2^+ . The individual lasers are now described in detail, followed by a discussion of the output of the laser system as a whole.

The Excimer Laser

Briefly, the operating principles of the excimer laser are as follows. An inert gas atom and a halogen gas atom form a short lived complex, called an excimer, through an electrical discharge. The excimer is formed in an excited state which dissociates upon decay, automatically creating the needed population inversion. The excimers are contained in a gas discharge vessel, where the lasing takes place. A plane mirror at the back of the vessel and a quartz flat at the front of the vessel, both aligned perpendicularly to the laser beam axis, form the resonant cavity. The quartz flat, with a reflectivity less than 5%, serves as the output coupler. The result is a cavity of very low q (fraction of the energy retained in the cavity per round trip of a circulating photon). The output is necessarily pulsed with a pulse length determined by the lifetime of the excimer complex. All excimer transitions currently in use range from the near UV to the VUV, and therefore an excimer laser can pump a large number of laser dyes without the need for frequency doubling. Because it operates solely in the UV, all optical components used in the excimer laser are made of fused silica. The spectrum of our excimer laser is broad, with a linewidth greater than about 10 nm, the output beam is highly divergent and is unpolarized. Because of the large gas vessel (50 liters) and high pressures (3 ATM) used, output energies of approximately 0.1 Joule per pulse can be achieved. (It should be noted that the optical characteristics of the laser output can be improved by placing the gas vessel inside a resonant cavity with a higher q , but at the expense of lower output pulse energies.) The feed gases

used in the excimer laser were Xe and Cl₂, forming the XeCl excimer that lases at 308 nm. Typical excimer laser output specifications are given in table (7.1) below. The pulse energy and average power listed are valid when Ne is used as the buffer gas. (He can also be used, but with lower pulse energies and average powers.)

Excimer Laser Output Specifications

Excimer	XeCl
Wavelength	308 nm
Pulse duration	8-10 nsec
Pulse energy	80-100 mJ
Repetition rate	20-100 Hz
Average power	4-10 Watts

Table (7.1)

The Dye Laser

In contrast to the excimer laser, the lasing medium of the dye laser consists of large organic molecules in solution. The dye molecules are optically pumped by the excimer beam and their subsequent fluorescence generates the laser pulse. In addition, the solvent plays a crucial role in three aspects. Through collisions between dye and solvent molecules, individual rovibronic levels of the dye molecules are broadened to the extent that the resulting absorption and fluorescence spectrum of the dye is continuous. Additionally, collisions between optically pumped dye molecules and the solvent help to create the population inversion in the dye; by rapidly (picoseconds) quenching higher vibrational levels of the upper electronic state, a population inversion is created between the lowest vibrational level of the excited state and various vibrational levels of the ground state. This quenching also has the effect of red shifting the fluorescence spectrum with

respect to the absorption spectrum. These three effects are crucial to the construction of a tunable source of coherent radiation, *i.e.*, a dye laser. The absorption and fluorescence spectra for Excalite 392A, dissolved in dioxane and measured with a Perkin-Elmer spectrophotometer and fluorometer are shown in figure (7.3) below. Incident radiation at 308 nm was used to generate the fluorescence spectrum in order to simulate excitation by the excimer laser. The red shift of the fluorescence spectrum is clearly seen. Also note that stimulated emission was obtained between approximately 380 and 400 nm, surrounding the peak of the fluorescence spectrum.

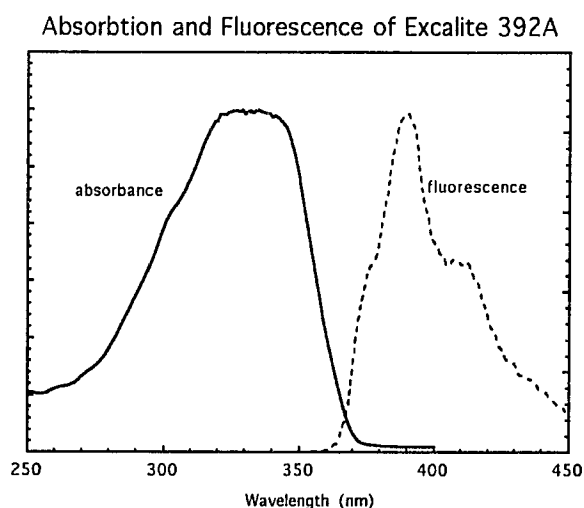


Figure (7.3)

The dye laser essentially consists of two cells, the oscillator and the amplifier, in which the excimer beam is absorbed by the dye solution. The laser pulse originates in the oscillator and is amplified in the amplifier. The excimer beam is split before it enters either cell with approximately 75% of the excimer power going into the amplifier. After being focused to a narrow line, the excimer beam enters each cell at right angles to the optical axis of the dye laser. In order to maximize the output power, the excimer beam is delayed before entering the amplifier cell so that there is maximum temporal overlap

between excimer beam absorption and the pulse from the oscillator. The delay is accomplished by a suitable optical path length of the excimer beam between the beam splitter and the amplifier cell. The dye solution is circulated in a closed loop by a single reservoir and pump. A segment of the loop consists of a heat exchanger that cools the dye solution.

The actual laser cavity of the EPD-330 is bounded by the output coupler at one end and a diffraction grating and tuning mirror arrangement at the other end, as shown in figure (7.4) below (Lumonics Inc., 1982). The output coupler is a 1° quartz wedge that acts either as a front or rear surface reflector. The diffraction grating is a flat 2400 lines/mm holographic reflection grating. The tuning mirror is a flat, front surface reflecting

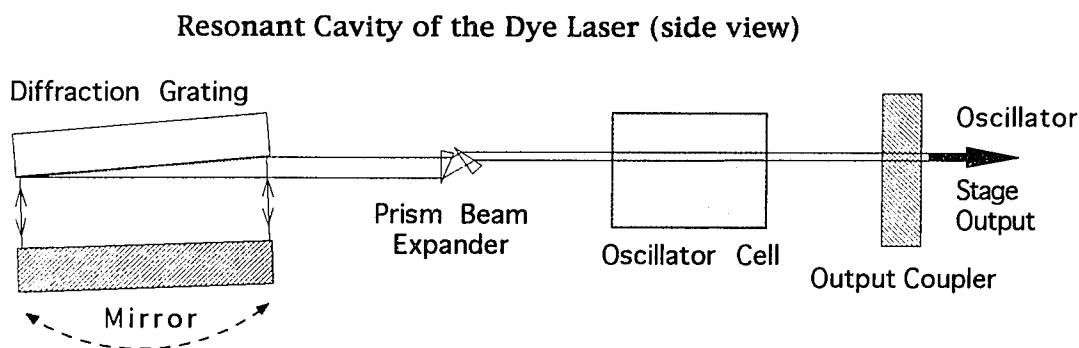


Figure (7.4)

mirror, mounted so that it can revolve about the midpoint of the grating, as shown. The grating and tuning mirror select the output wavelength in the following way. A light beam incident on the grating from the oscillator is diffracted onto the tuning mirror. The diffracted beam is dispersed in space according to its wavelength. Only that portion of the beam that strikes the mirror at right angles retraces its steps and is amplified; *i.e.*, the angle of diffraction of the outgoing light ray must equal the angle of incidence of the incoming light ray in order for amplification to occur. Wavelength selection

is accomplished by changing the angle of diffraction between the grating and the normal to the mirror by revolving the mirror about the grating. The tuning mirror, mounted on the end of a pivot arm, is revolved about the grating by turning a threaded rod which is itself turned by hand or by means of a stepper motor.

As shown, the angle of incidence of the light beam incident on the grating is very large, approaching 90° . This is to enlarge the projection of the light beam on the grating, which is proportional to $1/\cos(\alpha)$ where α is the angle of incidence. The function of the prism beam expander (PBE), shown between the oscillator and the grating, is to enhance this process by widening the beam before it reaches the grating. The primary reason to enlarge the projection of the light beam on the grating is that the resolving power of the grating is proportional to the number of grooves illuminated. The dye laser can be operated with higher output powers without the prism beam expander but with a concomitant increase in linewidth.

The reported linewidth of the EPD-330 is 0.2 cm^{-1} ($0.03 \text{ \AA}$) at a wavelength of 390 nm and the 85° standard angle of incidence (Lumonics Inc., 1982). The optical path length of the resonant cavity is approximately 25 cm , resulting in a longitudinal mode spacing of 0.020 cm^{-1} . The width of an individual mode is estimated to be 0.005 cm^{-1} , much less than the mode spacing (Young, 1994). However, when an average of many laser pulses is looked at, individual modes are not discernible and only a Gaussian envelope is seen. This is due to random fluctuations in the refractive index of the dye solution in the oscillator cell, which changes the optical path length and therefore the resonant frequency of the oscillator cavity. The 0.2 cm^{-1} linewidth, quoted above, is the FWHM of the gaussian envelope that results from averaging over many laser pulses (Lumonics Inc., 1994).

Laser Pulse Characteristics

The characteristic features of the dye laser pulse which determine its usefulness as a probe laser are: 1) signal to noise ratio, 2) overall pulse energy, 3) laser linewidth, 4) pulse duration, and 5) tunability (*i.e.*, the ability to reliably control and measure the laser wavelength). The first four features are discussed now, while a discussion of the laser tuning is deferred to the next chapter.

The spectra shown here were obtained using a SPEX model 500M 0.5 meter Czerny-Turner spectrometer and a Hamamatsu model R406 PMT, seated inside a liquid N₂ (LN₂) cooled housing. A minimum resolution of 0.2 Å (FWHM) was obtained with the narrowest slit widths (10μ). Figure (7.5) shows examples of the dye laser output under conditions where no lasing occurred. The resulting spectra represent background, or noise in the laser pulse. Curve (3), in which the tuning mirror was intentionally misaligned represents the most common background spectrum observed. The other curves are included to show unusual features. The primary phenomenon responsible for all the spectra shown in figure (7.5) is amplified spontaneous emission (ASE), which is caused by "accidental" lasing, or the formation of a (pseudo)resonant cavity that does not include the conventional wavelength selection elements; *i.e.*, the grating and tuning mirror. For example, the output coupler and either a window of the oscillator cell or the PBE are likely to form one or more such cavities. It is likely that the shape of the ASE spectrum shown in curve (3), specifically the minimum at approximately 3900 Å, is the result of the sum of two such cavities, whose (pseudo)resonant wavelengths are separated by approximately 30 Å.

Note that lasing action due to Littrow diffraction, in which the incident beam is diffracted back onto itself without being reflected by the tuning mirror, is possible in 2nd order and was, in fact, observed for certain positions

Dye Laser Background Spectra (oscillator only)

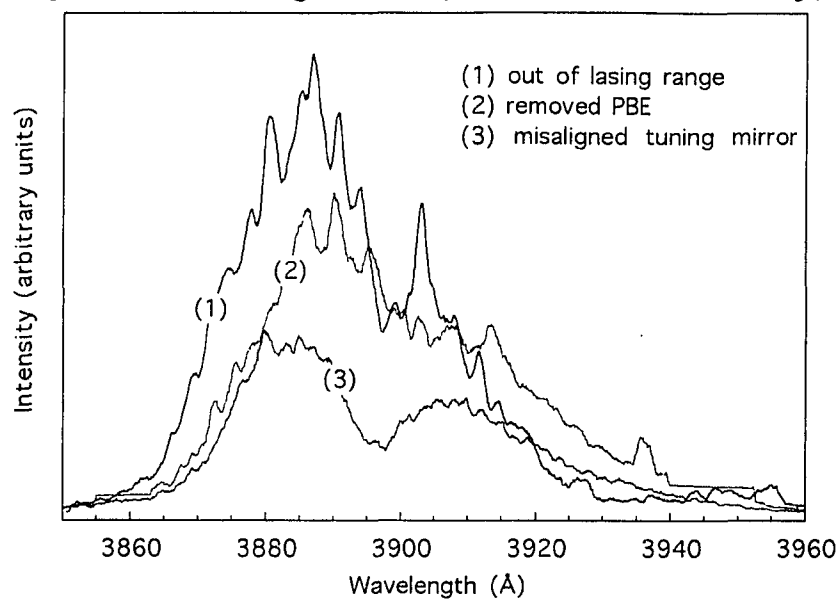


Figure (7.5)

of the elements associated with the oscillator cell. However, the wavelength of this Littrow lasing spot is at 415 nm, so that it cannot be responsible for the ASE spectra shown above. Curves (1) and (2) are the only examples where the minimum at 3900 Å is either much less pronounced or completely absent. The fact that curve (2) was obtained with the PBE removed suggests that it is responsible for the minimum at 3900 Å. However, curve (1), obtained with the PBE in place, also shows a minimum at 3900 Å which is not caused by the same phenomenon responsible for the majority of minima obtained in the ASE spectra, shown in curve (3). In fact, curve (1), obtained under proper alignment conditions but at a wavelength just beyond the usable lasing range of the dye, may be the result of competition between weak lasing and ASE modes.

Figure (7.6) below gives three examples of oscillator cell output under conditions of proper alignment, and with all necessary elements in place for lasing to occur. As shown, the lasing peak is superimposed on the background

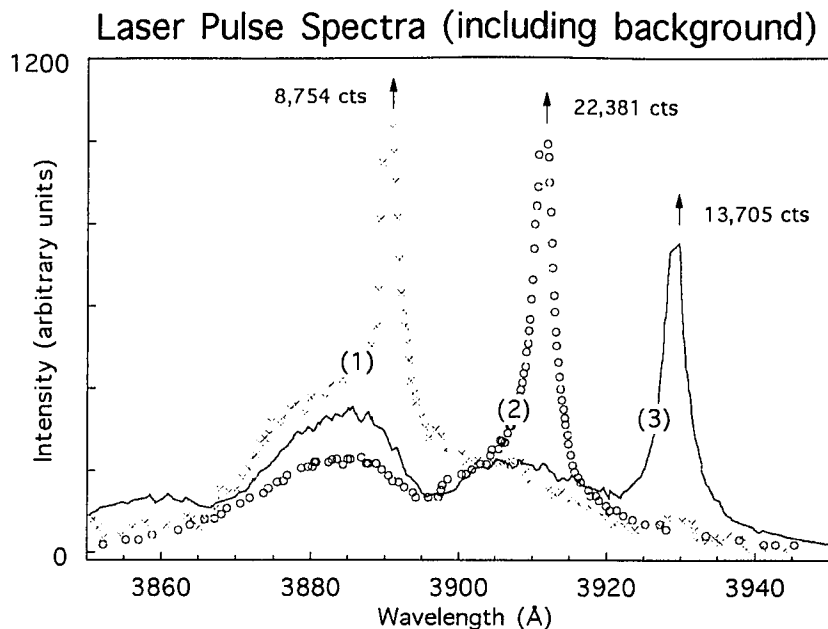


Figure (7.6)

in the output spectrum. Note that the actual lasing peaks are much higher; the peaks are not displayed in full in order to emphasize the structure where the peak merges into the background. This structure, or extended width at the base of the peak, is perhaps more clearly seen in figure (7.7) below, where laser pulses are shown with the background subtracted. Note that this is a

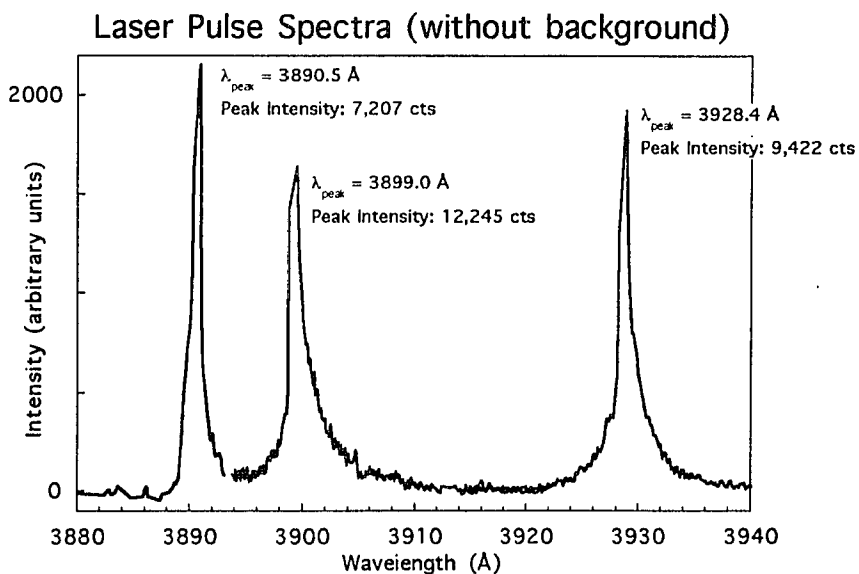


Figure (7.7)

composite figure; the three spectra were taken separately and grouped together later. Also, the peaks have again been truncated to show the structure at the peak base. This structure is worrisome for LIF studies where the narrow linewidth of the laser is needed to selectively pump spectral lines separated by a few tenths of an Ångstrom or even less. Figure (7.8) below compares the line shape of the dye laser output pulse with the output of a HeNe laser, which is known to have a "clean" spectrum. Both line shapes were measured with similar settings of the spectrometer (*i.e.*, slit widths), but very different laser parameters (wavelength, power, and beam diameter). The similarity in line shapes strongly suggests that the observed base structure is generated by the spectrometer itself - specifically by imperfect centering of the image of the laser spot on the grating - and is not inherent in the laser line shapes.

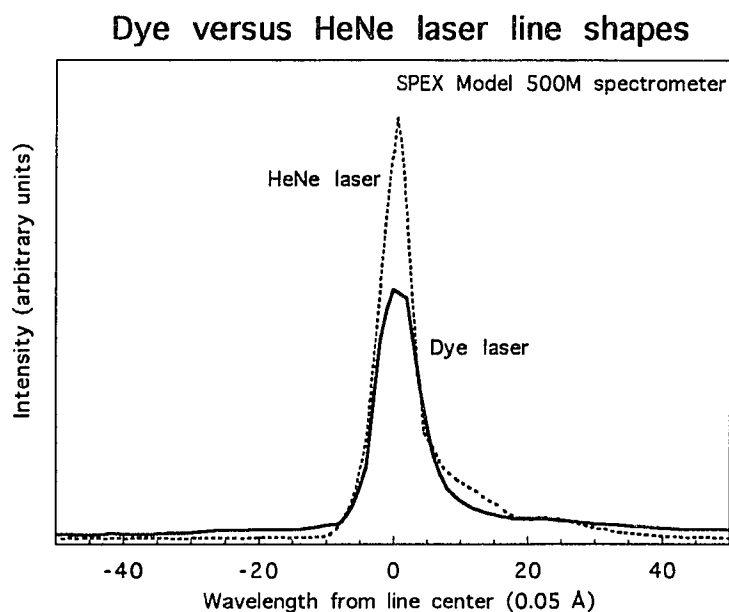


Figure (7.8)

Based on these findings, the following comments regarding the signal to noise ratio of the laser output pulse can be made. Signal to noise ratios, as

measured by taking the ratio of the net laser line peak (as shown in figure (7.7)) to the corresponding background (shown in figure (7.6)) ranged from approximately 1:4 to 1:1. It should be noted that these numbers by themselves, though they seem rather low, have little absolute meaning. What is important is to maximize the signal to noise ratio, however it is measured. It was discovered while using the Exalite 392A dye that the signal to noise ratio of the output pulse as well as the overall conversion efficiency, as measured by the ratio of dye laser output power to excimer laser input power, decreased as the repetition rate of the excimer laser increased. This effect, caused by an incomplete dye replacement in the dye cells between excimer pulses, due to an inadequate pumping speed of the dye recirculator, limited the useful excimer repetition rate to a maximum of 40 Hz. Furthermore, it was discovered that the signal to noise ratio of the dye laser output pulse increased as the focus of the excimer beam into the dye cells was weakened; that is, the intensity of the excimer beam as it passed through the lasing region of the dye cells was decreased. This was accomplished simply by moving the focusing lenses closer to their respective dye cells. This combination of lower excimer repetition rates and weaker excimer beam focusing resulted in the highest signal to noise ratios and conversion efficiencies attained and was used for all the LIF studies presented here.

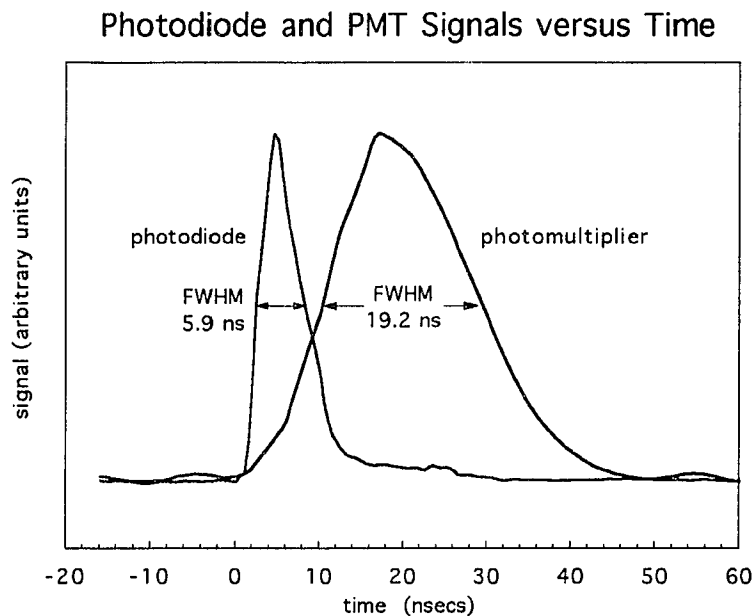
Overall pulse energies were measured with a Laser Probe model RjP-637 laser pulse energy (LPE) meter which, in its usual arrangement, reports laser pulse energies averaged over a range between 20 and 100 pulses. A maximum of approximately 300 μJ per pulse was measured with the LPE meter behind the vacuum chamber. Laser pulse energies were measured in this way, behind all the apertures and mirrors in the dye laser path in front of the vacuum chamber as well as the electron beam monochromator inside the vacuum

chamber, in order not to overestimate the intensity of the laser beam that passes through the interaction region. Laser pulse energies approximately 10 times higher could be measured at the dye laser exit port with no limiting elements in front of the LPE meter.

Laser linewidths were measured with the SPEX spectrometer, as mentioned above. Examples are shown in figure (7.7). The measured 0.2 Å (FWHM) linewidths represent the minimum resolution of the spectrometer and not the true linewidth, which is reported to be 0.03 Å (0.2 cm^{-1}). Additionally, in a preliminary set of experiments which will be discussed in more detail in the next chapter, the laser linewidth was measured using the optogalvanic effect. These measurements provided an upper limit to the true laser linewidth. The linewidths measured optogalvanically ranged from 0.048 Å to 0.26 Å, but the upper value is the result of power broadening. Therefore, with Doppler broadening taken into account, the upper limit of the laser linewidth is taken to be 0.04 Å. This compares favorably with the manufacturer's specification of 0.03 Å.

Lastly, shown below in figure (7.9) are time profiles of the dye laser output pulse as measured by a fast phototube (Hamamatsu R1193U) and photomultiplier tube (PMT) (Hamamatsu R1104), and recorded with a digital storage oscilloscope (Lecroy 9310M). The phototube had a response time of a few hundred picoseconds and thus represents the true temporal profile of the laser pulse. The PMT used was attached to the vacuum chamber as shown in figure (7.1) and was the detector utilized in all LIF studies. Its response time, given as 15 ns by the manufacturer, is longer than the true laser pulse duration which accounts for the discrepancy in pulse shapes. Note that the photons responsible for the temporal profile given by the PMT come from laser light which is scattered from various elements inside the vacuum

chamber. In particular, note the approximately 20 ns decay time of the PMT pulse. During this time the PMT is unavailable to detect LIF photons. As will be seen later, care has to be taken to ensure that this minimum 20 ns "dead" time is not enlarged by other experimental conditions.



The Electron Beam

A schematic diagram (approximately 2:1 scale) of the elements used to create, collimate, bend, and focus the electron beam is shown in figure (7.10) below. Briefly, the bare tungsten filament is resistively heated to about 3000°K using a current between 2.2 and 2.5A, causing thermionic emission (Moore *et al.*, 1983). The electrons thus released are extracted from the filament region and focused onto the entrance of an electrostatic energy analyzer (Comstock model AC-900) by three aperture lenses. The electrons leaving the analyzer are focused into the interaction region by an Einzel lens. An end cap, part of the shielded box enclosing the entire assembly, is kept at

ground potential to avoid field penetration into the interaction region.

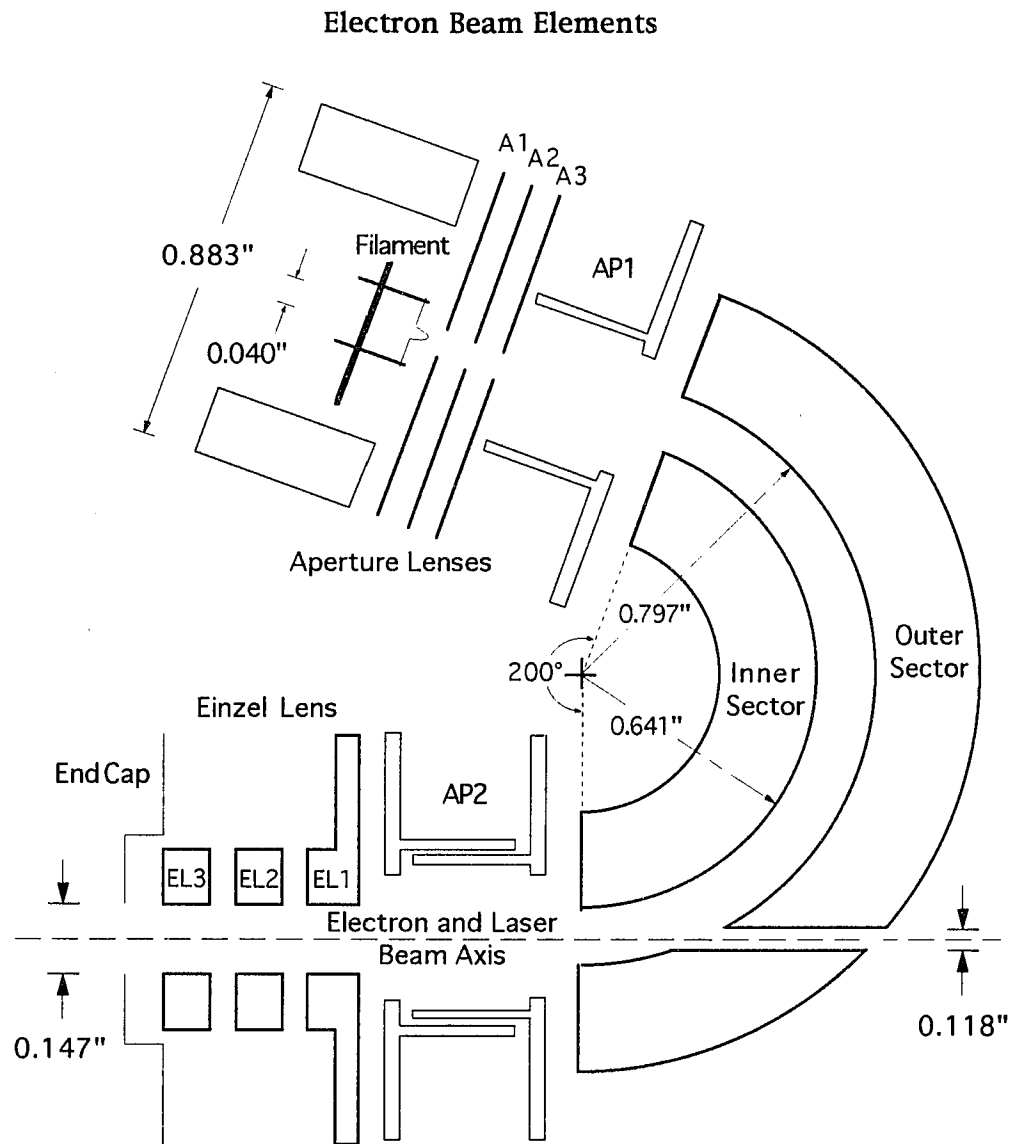


Figure (7.10)

The electron beam was designed with two objectives in mind: 1) to enable a geometry in which there is maximum overlap of the gas, laser and electron beams, and 2) to maximize the electron beam current in order to create as many targets for LIF detection in the interaction region as possible. In order to maximize the overlap between the electron and laser beams, it was decided to

make them collinear. For this reason, the Comstock electrostatic energy analyzer was modified by drilling a 3 mm hole in the outer sector, thus allowing the laser to pass through. In addition, the input and output apertures normally used with the analyzer were eliminated, allowing a larger electron beam cross section, albeit with a poorer energy resolution. The analyzer, without apertures, acts merely as a bender, thus allowing collinear electron-laser beam axes. The energy spread of electrons passing through the endcap is estimated to be 0.75 eV, which is determined solely by the energy spread of the electrons thermionically emitted from the filament.

In addition to using the analyzer without apertures as described above, it was found that a significant increase in electron beam current could be obtained by increasing the transmission energy (the mean energy of an electron passing through the analyzer). When energy resolutions of 0.1 eV or better are desired, transmission energies as low as 10 eV have to be used. In the present experiment we used transmission energies of 80 eV or higher. Using a filament current of 2.5 A and a transmission energy of 210 eV, a maximum beam current of approximately $30 \mu\text{ A}$ was obtained.

The electron beam was collected in a Faraday cup that had three electrically isolated elements, which allowed the beam divergence as well as the total current to be measured. The two outer elements were coaxial cylinders that each had a 5 mm diameter hole in the back, coaxial with the electron-laser beam axis, while the third element was a rectangular plate parallel to the electron-laser beam axis, placed inside the second element just beneath the hole. The outer cup was kept at ground potential while the other two elements were biased positively with respect to ground, typically +9 volts for the middle cup and +45 volts for the small inner plate. With this arrangement the laser was allowed to pass through unobstructed while the

electron beam was attracted to and collected by one of the Faraday cups. (The laser subsequently exited the vacuum chamber.) In addition, the bias voltages served to minimize the scattering of electrons back into the interaction region, known as backscattering. To minimize backscattering even further, the outer Faraday cup was made approximately three inches deep, which had the additional effect of preventing the fields generated by the bias voltages from penetrating into the interaction region.

The electron beam currents on the individual Faraday cups were monitored using two Keithley model 610C electrometers and one Keithley model 485 picoammeter. Under operating conditions (the gas beam present and the lens voltages optimized for maximum beam current and minimum beam divergence), with a total beam current of $14 \mu\text{ A}$, the inner cup measured $11 \mu\text{ A}$, the middle cup $3 \mu\text{ A}$, and the outer cup approximately $0.1 \mu\text{ A}$. With higher total beam currents, the divergence increased. During the course of operation, over a period of two hours or longer, the drift in the total beam current as well as the individual Faraday cup currents were kept to 10% or less by periodically checking and, if necessary, manually adjusting lens element voltages.

Computer simulation of the electron beam focal properties

The final element of the electron beam system before the interaction region is the Einzel lens, designated EL1, EL2, and EL3 in figure (7.10) above, whose purpose is to form a collimated and focused beam in the interaction region. Actually, AP2 (the exit aperture of the bender), EL (the Einzel lens), and EC (the end cap) form a five element lens whose focal properties are unknown. For this reason, the focal properties of these five elements were investigated using the SIMION electrostatic lens ray tracing program (Dahl *et al.*, 1988).

Specifically, using SIMION, the focal length of the lens was calculated as a function of the voltages on the various elements which, except for constraining EL1 to be equal to EL3 and EC to be zero, were treated as independent variables. As expected from a consideration of the geometric aberrations affecting electrostatic lenses, it was found that even for fixed voltages, the distance from the lens at which an electron crossed the symmetry axis, the focal length, still depended on the starting position of that electron (*i.e.*, the focal length of the lens depended on the initial distribution of electrons entering it). Therefore, in order to obtain useful information concerning the focal properties of the lens, it was necessary to assume an initial distribution of electrons (beam shape) entering AP2. A Gaussian distribution about an axis coincident with the symmetry axis of the lens was chosen because of its simplicity and versatility: only a single parameter, namely the standard deviation σ , which became another independent variable, distinguished a narrow beam from a wide beam. The focal length for a given voltage configuration could then be calculated in the following manner. Initial electron positions were distinguished by their initial perpendicular distance from the symmetry axis ρ_i and initial trajectories were chosen parallel to the symmetry axis. Ten initial starting positions were used in the calculation, labeled ρ_i , and bounded by the symmetry axis and maximum lens radius. Next, the focal length x_i , for each ρ_i was computed using SIMION. Each initial trajectory was then weighted according to P_i , where $P_i = \rho_i e^{-\rho_i^2/2\sigma^2}$ and the overall focal length for the voltage configuration computed using $\bar{x} = \sum x_i P_i / \sum P_i$.

Figure (7.11) below shows the results obtained under the following conditions: AP2 is fixed at -80 Volts, EC is fixed at 0 Volts, and σ , the standard deviation of the initial electron distribution, is taken to be 1 lens diameter.

The focal length is plotted versus V_2/V_1 , the ratio of electron kinetic energy at EL2 to the electron kinetic energy at EL1, which is the independent variable used in standard Einzel lens plots. In addition, the focal length, shown parameterized by $EL1/3$, varies slightly for different values of this parameter in contrast to standard Einzel lenses. This is expected and simply the result of

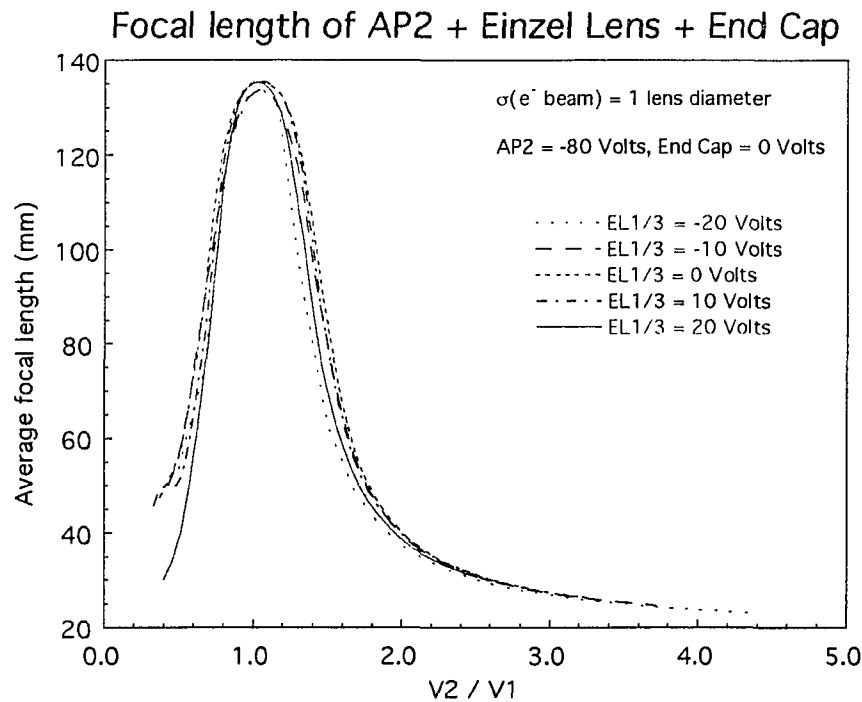


Figure (7.11)

adding the two elements, AP2 and the EC, to the Einzel lens. (A close examination reveals that the curve lying closest to $EL1/3=-20$ is $EL1/3=20$ and the curve closest to $EL1/3=-10$ is $EL1/3=10$ which implies that the effects of AP2 and EC almost cancel each other.) Not shown in figure (7.11), for each curve corresponding to a different value of the parameter $EL1/3$, when V_2/V_1 is close to 1 the focal length is greater than the 140 mm upper limit used in the simulation. Also note that the origin of the focal length scale is the left edge of AP2; a value of 31 mm indicates focusing just past the end cap.

Figure (7.12) below, for which $AP2 = -80$ Volts, $EC = 0$ Volts, and $EL1/3$ is fixed at 20 Volts, shows the effect of the initial electron distribution on the average focal length. As shown, for each value of $V2/V1$ the focal length is longer for the narrower beam. This reflects the geometrical aberration of the

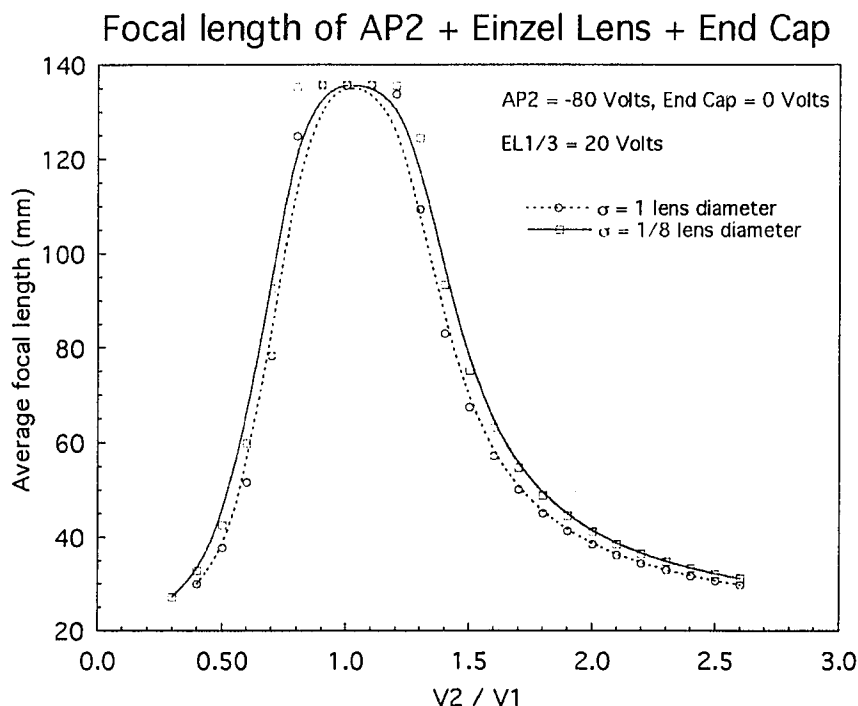


Figure (7.12)

lens in which electrons originating near the center of the lens are bent less sharply than electrons near the edge. This is more clearly reflected in figure (7.13) below, which is an actual ray trace provided by SIMION using the same parameters as in figure (7.12) above, and additionally $EL2$ is fixed at 50 Volts. However, in the ray trace shown below no initial electron distribution is assumed (*i.e.*, there is no weighting of the different initial trajectories). As shown, owing to geometrical aberration, there is no single focal point, only a plane where the beam diameter is a minimum (called the beam waist), whose location is very nearly given by the average focal lengths plotted in figure

Electron Trajectories Calculated using SIMION

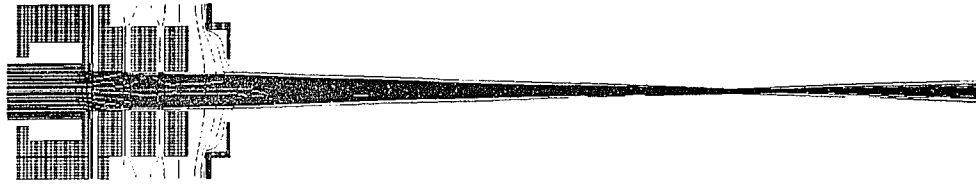


Figure (7.13)

(7.12) above. Figure (7.14) below, based on the same trajectories shown above, is an enlargement of the region near the "focal point". The dashed lines are simply the extremum

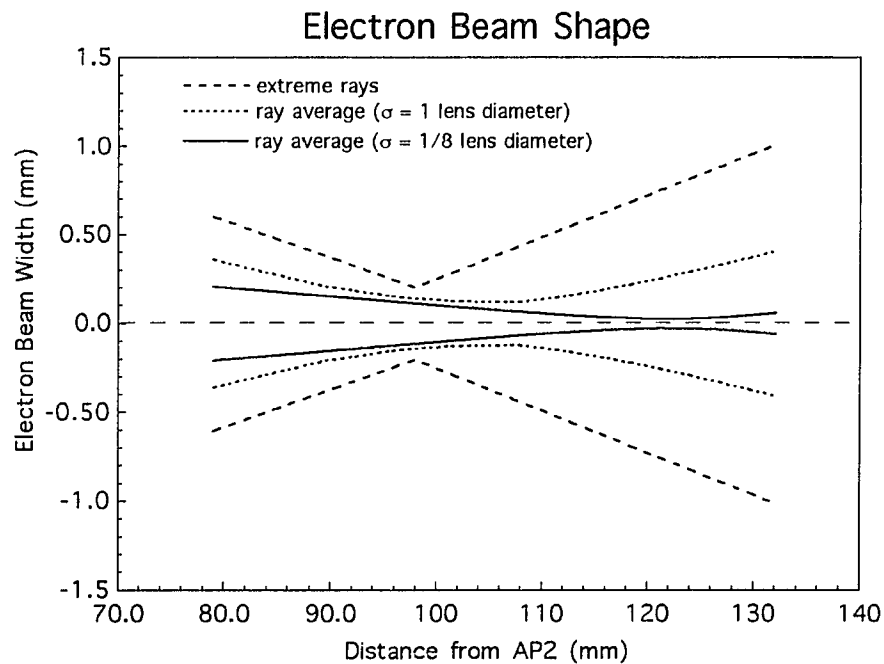


Figure (7.14)

rays from figure (7.13) above, while the solid and dotted curves give the average value of ρ as a function of the distance downstream from the lens. The portion of each curve below the x-axis is simply the mirror image of the curve above the x-axis and is drawn only to visualize a possible beam shape. The minimum width of the initially wider beam ($\sigma = 1$ lens diameter) is about 5

times that of the initially narrower beam ($\sigma = 1/8$ lens diameter) and is located closer to the end of the lens, consistent with figure (7.12).

It should be emphasized that the results of this simulation, presented in figures (7.11) to (7.14) above, do not give the total picture of the electron beam, so that the results should be used with care. For example, the variation of the total beam current with lens voltage was not considered in the simulation. Specifically, the same focal length may be obtained with more than one lens element voltage combination, but those different voltage combinations may result in different total currents. (This was found experimentally.) The lens element voltage combinations shown above were chosen first because they resulted in large beam currents and second, because they produced useful focal lengths. Additionally, it was shown how the initial distribution of electron trajectories affected the focal properties of the lens, but the simulation could not determine that distribution. These considerations limited the use of the results of the simulation to the formulation of guidelines, giving the approximate location and shape of the electron beam with different lens element voltage combinations. In practice, the guidelines obtained from the computer simulation were used in conjunction with other, empirically deduced guidelines which included the following: only using the positive side of the Einzel lens ($V_2/V_1 \geq 1$), and maintaining EL1/3 between 10 and 20 volts higher than AP2.

The Photon Detection System

The photon detection system consists of a light collection system, an interference filter, a detector and its associated electronics, and a gated photon counter. The light collection system was designed to maximize the collection of radiation originating from the interaction region and the transport of this

radiation to the photon detector while minimizing the amount of scattered laser light that reaches the detector. The interference filter (Andover Corporation 430-FS10-50) is used to select a single vibrational band for detection, in the present experiment, the $N_2^+ B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+(0,1)$ band. The photon detector, a Hamamatsu model R1104 photomultiplier tube (PMT) is used in conjunction with amplifier and discriminator electronics to count the photons transmitted by the interference filter. In order to decrease thermal noise, the PMT is maintained at approximately -40°C by placing it inside a thermoelectrically cooled housing (Products for Research model TE175RF). Lastly, time resolved fluorescence studies were made possible by the use of a Stanford Research model SR400 gated photon counter which, after suitable amplification and discrimination, accumulates the pulses from the PMT that arrive within a specified time window, or gate. Typically, the SR400 was used with a 5 ns gate width whose opening was incrementally delayed 5 ns after each set of 1000 laser pulses. In this way the lifetime of the $N_2^+ B^2\Sigma_u^+$ state could be measured.

The light collection system, shown below in figure (7.15), consists of an aperture and primary lens that are located inside the vacuum system, a window that serves as the vacuum-atmosphere seal, and a secondary lens located outside the vacuum system. Both lenses are plano-convex. The primary lens has a 50 mm focal length and a 40 mm diameter and the secondary lens has a 75 mm focal length and a 50 mm diameter. Also shown are the interference filter and the detector surface upon which the collected light is focused. For extended transmission into the UV, below approximately 200 nm, the lenses and the window are made of uncoated synthetic fused silica (Melles Griot and Heraeus Amersil). All optical components located outside the vacuum system, including the detector, are situated inside a telescopic

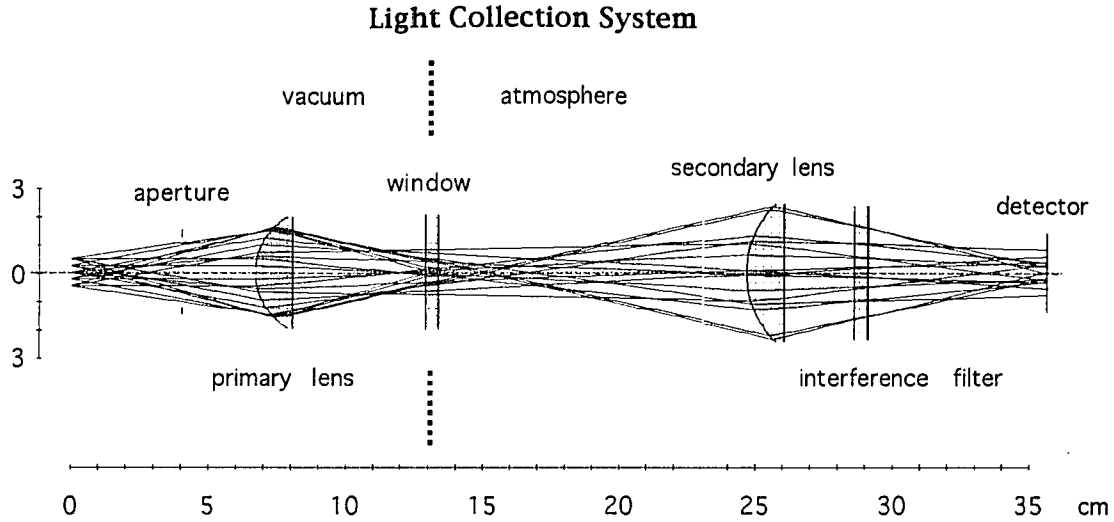


Figure (7.15)

aluminum tube that is not shown in figure (7.15). The aluminum tube, made light tight by the use of o-ring seals at all metal-metal interfaces, ensures that no stray light reaches the detector and, at the same time, increases the efficiency of the light collection system by reflecting light rays back toward the optical axis that would otherwise be lost. Similarly, the primary lens, located inside the vacuum chamber is housed in another telescopic aluminum tube that extends from the window to the aperture. The inner surface of this tube is blackened with Aerodag to absorb scattered laser light. Since the scattered laser light and any other stray light comes from all surfaces inside the vacuum chamber, it has a much higher probability of striking the blackened aluminum tube than the radiation which originates from the interaction region, located in the center of the vacuum chamber.

The detection efficiency of the light collection system is given by

$$E(\vec{r}) = \frac{d\Omega(\vec{r})}{4\pi} T(\vec{r}), \quad (7.1)$$

where $\vec{r}$ specifies the location from which a light ray originates, $d\Omega(\vec{r})/4\pi$ is the solid angle subtended by the light collection system at $\vec{r}$, determined by

the primary lens and aperture, and $T(\bar{r})$ is the throughput, or the ratio of the amount of light reaching the detector to the amount of light reaching the primary lens. In order to maximize $d\Omega(\bar{r})/4\pi$, the primary lens was chosen with a low f-Number (1.25) and a large diameter (40 mm). The throughput, $T(\bar{r})$, was maximized by using large diameter optical elements and by optimizing their placement. The three quantities $E(\bar{r})$, $d\Omega(\bar{r})/4\pi$, and $T(\bar{r})$ are shown in figure (7.16) below as a function of position along the electron beam axis (*i.e.*, along the y-axis shown in figure (7.2)). $d\Omega(\bar{r})/4\pi$ was calculated by evaluating the integral $\iint \hat{n} \cdot d\bar{A}/R^2$ where $\hat{n}$ is the unit vector originating at $\bar{r}$ and specifying the direction of a ray of light, $d\bar{A}$ is an element of surface area on the primary lens, R is the distance between the specified points, and the limits of integration depend on the location of the source point. The throughput, $T(\bar{r})$ was calculated using the BEAM2 (Stellar Software, 1989)

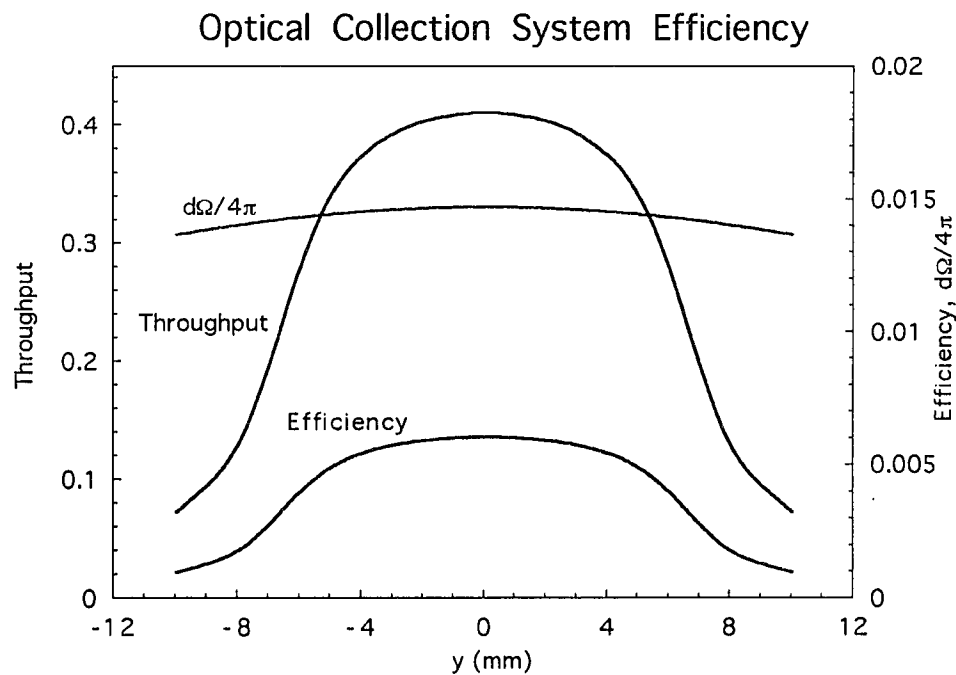


Figure (7.16)

optical ray tracing program in which light rays whose directions were

randomly generated were traced through all optical elements shown in figure (7.15), and the throughput was obtained by taking the ratio of the number of rays reaching the detector to the number of rays passing through the aperture. (This assumes an isotropic radiation pattern.) Also included in calculating the throughput were the reflection and absorption losses of the lenses and windows through which the detected light rays passed.

The interference filter, with a central wavelength of 432.5 nm and a bandpass of 10.3 nm (FWHM), was chosen to transmit the $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+(0, 1)$ band of N_2^+ (bandhead at 427.8 nm). The detection efficiency of the interference filter is determined by its transmission probability, which was supplied by the manufacturer and is shown below in figure (7.17). Also shown is the rotationally resolved spectrum of the $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+(0, 1)$ band of N_2^+ . The relative intensities of the individual rotational lines were obtained using

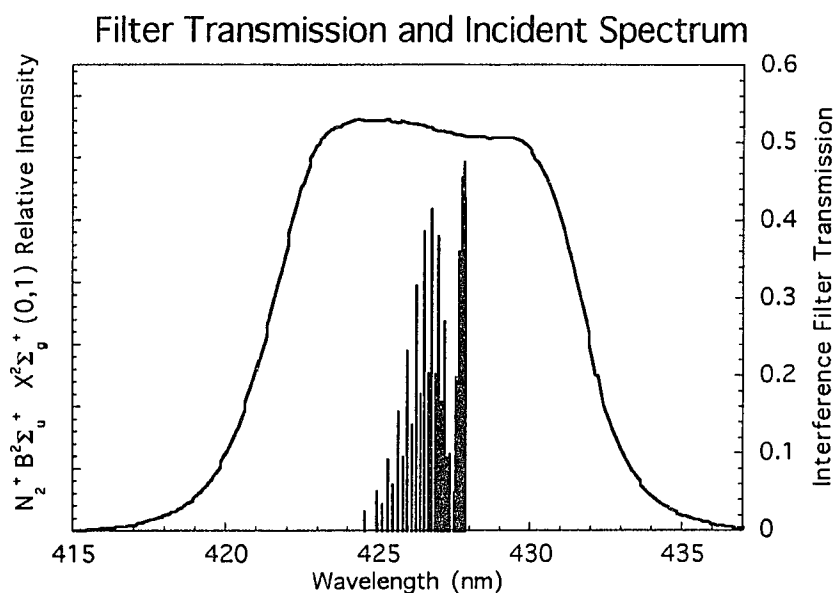


Figure (7.17)

dipole line strengths to model the electron impact excitation process. (Only slightly different intensities were obtained using quadrupole line strengths.)

(Zetner *et al.*, 1988). In order to shift the central wavelength from 432.5 nm down to the 427.5 nm shown above, the filter was angle tuned, or tilted with respect to the optical axis, at approximately 13° . With this experimental arrangement, the transmission of the filter is very nearly constant over the entire range of the $N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)(0,1)$ spectrum, even when the convergence of the bundle of light rays incident on the filter is taken into account.

The Hamamatsu model R1104 photomultiplier tube (multialkali photocathode and 500U spectral response curve) was chosen to provide a high detection efficiency in the UV. The quantum efficiency of the photocathode, the ratio of incident photons to ejected photoelectrons, is 18.5% at 427 nm

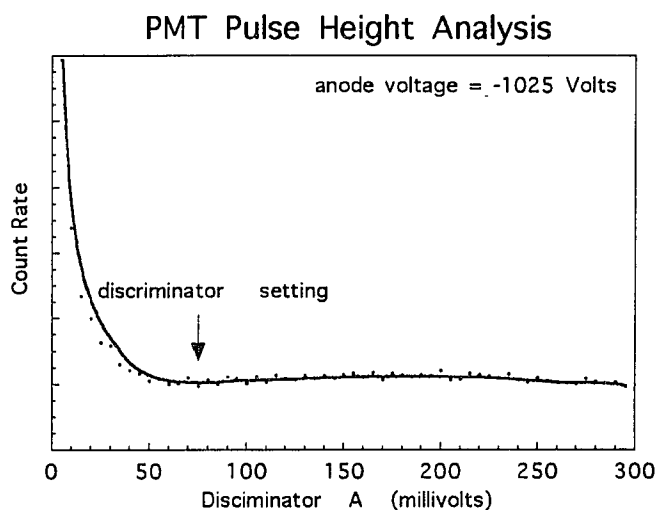


Figure (7.18)

(Hamamatsu Corp., 1985) and is very nearly constant over the wavelength range of the $N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)(0,1)$ spectrum. The optimal anode high voltage (-1025 V) and pulse height discriminator setting (-75 mV) were determined by a pulse height analysis of the PMT output pulses, shown above in figure (7.18). The dark count rate was approximately 20 counts/s when the PMT was maintained at -40°C .

The Gas Beam

The gas beam was formed using a multicapillary nozzle that consisted of 45 individual channels arranged in a 9 x 5 rectangular array. Each channel is 0.150" (0.3810 mm) long by 0.020" (0.0505 mm) in diameter and the separation between each channel is 0.032" (0.8128 mm). The multicapillary nozzle is positioned approximately 4 mm above the electron beam axis with the long axis of the nozzle parallel to the electron beam axis. Also, the electron beam and gas beam axes are perpendicular to each other, as shown in figure (7.2).

The number density of gas targets in the interaction region is determined by the total rate of flow of gas through the nozzle, referred to as the throughput, and the distribution of the flow as a function of the polar angle with respect to the nozzle axis, referred to as the beam shape. The throughput and beam shape depend on the type of flow through the nozzle, which is determined by the ratio of the mean free path of a gas molecule entering the nozzle to the nozzle diameter (Knudsen number). Finally, the mean free path is inversely proportional to the pushing pressure behind the nozzle, which typically was 0.5-0.6 Torr, although pressures up to 1 Torr were used. The different kinds of flow and their respective pressure ranges are listed in table

**N₂ flow through the Nozzle used in
the Triple Beam Apparatus**

Pressure (Torr)	Flow Regime	Flow proportional to
0 to 0.1	molecular	p
0.1 to 10	intermediate	p to p ²
> 10	viscous	p ²

Table (7.2)

(7.2) above for N₂ gas flowing through the nozzle described here. As shown, the typical pushing pressures used in the present experiment fall into the

intermediate flow regime, in which the dependence of the throughput on the pushing pressure gradually varies from the linear dependence found in the molecular flow regime to the quadratic dependence found in the viscous flow regime. The beam shape in the present experiment is also intermediate between the shape found in the molecular and viscous flow regimes.

In order to make a quantitative estimate of the number density of N_2 molecules in the interaction region, calculations were made utilizing a model described in (Giordmane *et al.*, 1960). Since this model is valid in the molecular flow regime only, the comparisons with experimental data, which will be made in the next section, will be made only with the pushing pressure below approximately 0.1 Torr. The gas number density curves shown below in

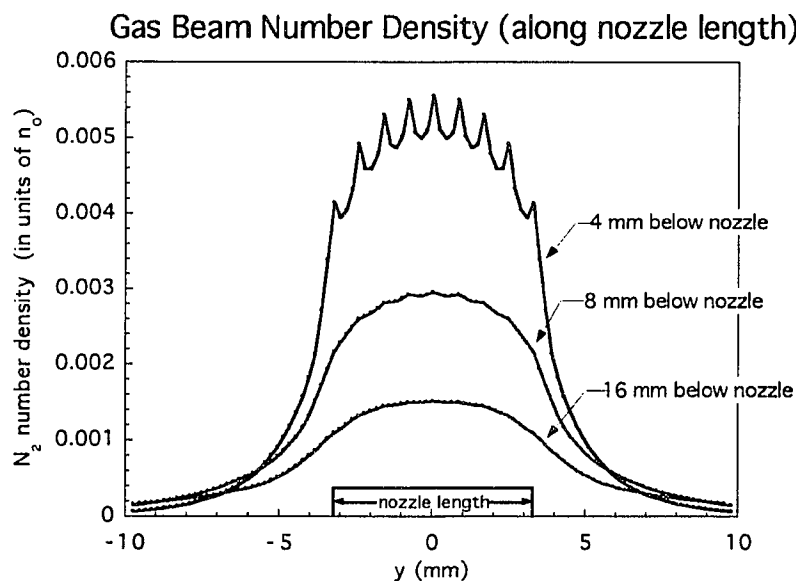


Figure (7.19)

figures (7.19) and (7.20) show the results of these calculations. The curves refer to the flow of N_2 molecules through the multicapillary nozzle described here. They were obtained by summing the contribution from a single channel over all 45 channels in the multicapillary array. Each figure gives the

number density of N_2 molecules in units of n_0 , the number density behind the nozzle, at three different heights below the nozzle. As shown, the x-axis is parallel to the nozzle width, the y-axis is parallel to the nozzle length, and the origin of coordinates (the point $x=0, y=0, z=0$) coincides with the geometric center of the nozzle. The structure in the curves labeled "4 mm below nozzle" results from contributions from individual channels, which are still distinctly recognizable at this height but are smeared out at heights of 8 mm and 16 mm below the nozzle.

While ab initio calculations of the throughput and shape of molecular beams formed by gas flowing through long tubes are known to be only approximate, with different authors reporting significantly different results (see for example Zugenmaier, 1965 and Olander *et al.*, 1970), there are some important conclusions that can be drawn from figures (7.19) and (7.20) that

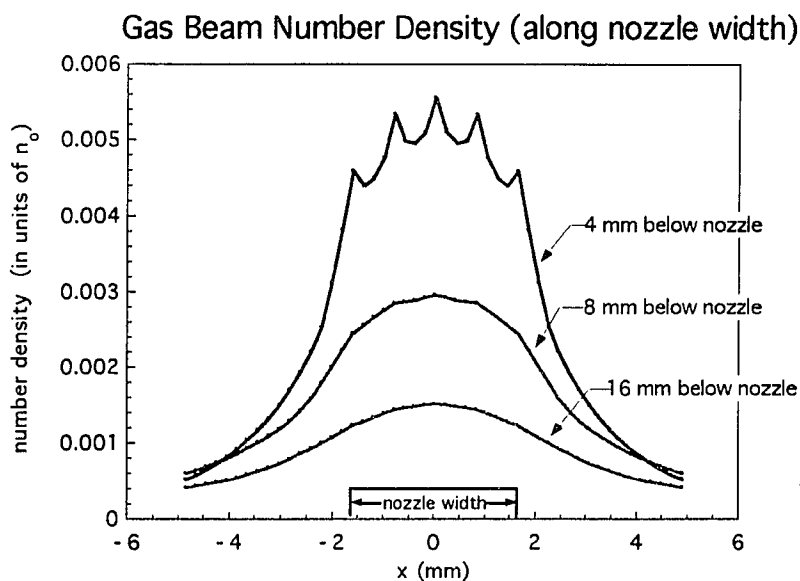


Figure (7.20)

will not change if a different model is used for the calculations. First, the average intensity near the center of the nozzle varies inversely with the

height below the nozzle, in contrast to the customary inverse square law. This is because the nozzle is a multicapillary nozzle and we are using heights below the nozzle which are of the same order as the overall dimensions of the nozzle. Far from the nozzle the intensity varies according to the usual inverse square law. Second, the intensity is nearly constant along any line perpendicular to the electron beam axis (constant y and z) where the electron and gas beams intersect ($|x| \leq 1$ in figure (7.20)). Taken together, these conclusions imply that the intensity of the gas beam is nearly constant over the cross section of the electron beam. This finding will be useful when estimating the overlap integral of the gas and electron beams.

VIII. Optogalvanic Calibration and Linewidth Measurement

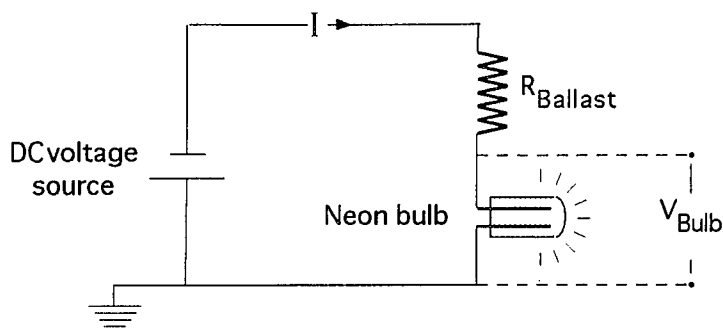
Introduction

As previously mentioned, a set of experiments was performed in which laser system output pulses were detected using the optogalvanic effect. In these experiments the wavelength of the dye laser was scanned and the resulting optogalvanic signal was recorded as a function of the dye laser wavelength. The resulting spectra consisted of discrete lines whose positions correspond to well known atomic transitions and whose shapes are a convolution of the optogalvanic and laser line shapes. Therefore, these spectra provided absolute wavelength markers that were used to calibrate the wavelength of the laser system and test the linearity of the dye laser tuning mechanism. In addition, the lineshapes measured this way provided an upper limit to the laser linewidth. These experiments are discussed in the following paragraphs.

Briefly, the optogalvanic effect reveals itself by the presence of a change of the impedance of a discharge, induced by resonant radiative transitions between excited states of one or more species making up the discharge. Both positive and negative impedance changes are possible. The impedance changes as a result of a change in the net ionization rate caused by changes in the population of excited states that contribute to the ionization (Goldsmith *et al.*, 1981). In the present case the discharge consisted of a miniature bulb containing Helium and Neon (Radio Shack) at a low pressure, connected to a D.C. voltage source as shown in figure (8.1) below. A portion of the dye laser output was passed through the bulb between the two electrodes. The wavelength dependent change in impedance was detected by measuring the voltage across the bulb as the stepper motor controlling the dye laser wavelength was incremented in regular steps. The maximum voltage change

at the position of a resonance was approximately 1.7 Volts and the bulb recovery time was approximately $50 \mu s$.

Optogalvanic Circuit and Operating Parameters



Operating Parameters

V_{DC}	200 Volts
$R_{Ballast}$	59.1 $k\Omega$
I	2.5 mA
V_{Bulb}	55 Volts
R_{Bulb}	24 $k\Omega$

Figure (8.1)

The laser pulses, stepper motor increment, and data acquisition were initiated by a laboratory computer which controlled the entire experiment. The analog to digital converter and Control Pulse unit shown were part of an IBM data acquisition card located inside an 80386SX IBM compatible computer. The pulse generator, shown below, allowed a user-adjustable delay between the trigger pulse and the optical laser pulse that could be measured with a

Apparatus Used for Optogalvanic Detection

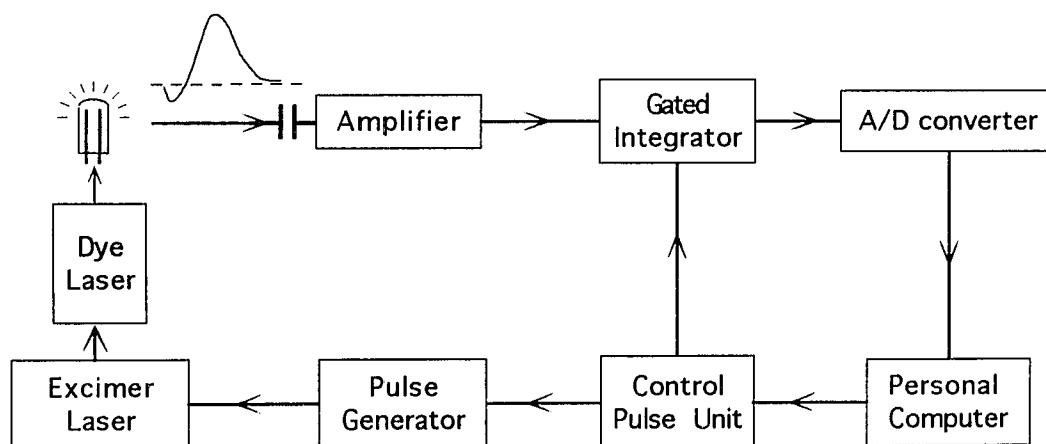


Figure (8.2)

phototube and an oscilloscope. The signal voltage, $V_{B_{ulb}}$, was capacitively coupled to the amplifier so that only the laser-induced change in voltage was measured. The output of the gated integrator (Evans model 4130A) was a voltage proportional to the time integral of its input. The integration start and stop times were determined by the opening and closing of the gate, which, in turn were controlled by pulses from the computer. The delay between the laser pulse and the opening of the gate and the width of the gate were preset to ensure that the entire optogalvanic signal was "captured" by the gated integrator. The output of the gated integrator was digitized by the A/D converter and stored in the computer. The dye laser scan rate (the stepper motor increment per data point) and the number of laser pulses averaged per data point were input parameters to the computer program controlling the entire data taking process. The data shown in figure (8.3) below were obtained by incrementing the stepper motor in units of 10 steps per data point, corresponding to 0.02 Å between data points. In addition, 10 laser pulses were

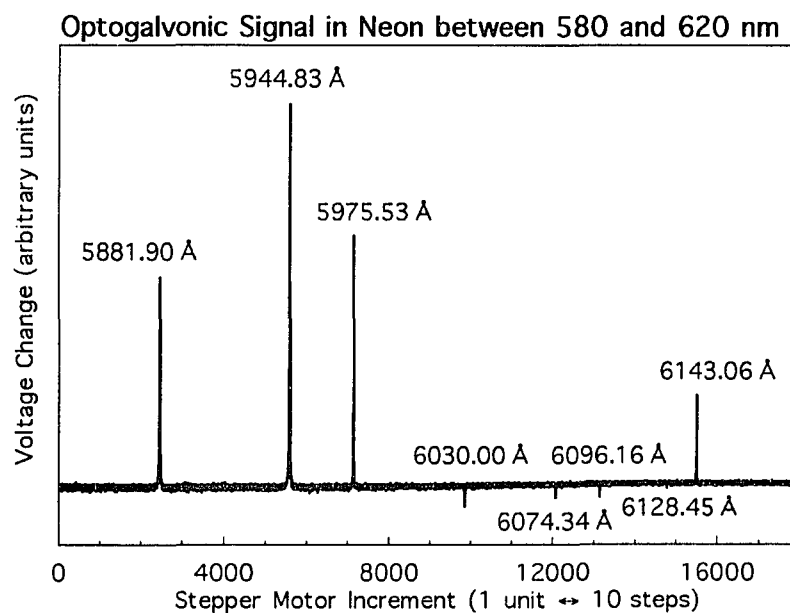


Figure (8.3)

averaged per data point resulting in a total acquisition time of just under three hours.

Figure (8.3) above shows the optogalvanic signal between 580 and 620 nm obtained with the Neon bulb, and table (8.1) below lists the transitions corresponding to the lines identified in the optogalvanic spectrum. All lines

Transitions Corresponding to the Optogalvanic
Spectrum in Neon between 580 and 620 nm

Wavelength (Å)	Transition	Polarity
5881.90	$3s[3/2]_2 \rightarrow 3p'[1/2]_1$	positive
5944.83	$3s[3/2]_2 \rightarrow 3p'[3/2]_2$	positive
5975.53	$3s[3/2]_2 \rightarrow 3p'[3/2]_1$	positive
6030.00	$3s[3/2]_1 \rightarrow 3p'[1/2]_1$	negative
6074.34	$3s[3/2]_1 \rightarrow 3p[1/2]_0$	negative
6096.16	$3s[3/2]_1 \rightarrow 3p'[3/2]_2$	negative
6128.45	$3s[3/2]_1 \rightarrow 3p'[3/2]_1$	negative
6143.06	$3s[3/2]_2 \rightarrow 3p[3/2]_0$	positive

Table (8.1)

originate from the $2p^5 3s$ configuration of Neon, which consists of four levels, two of which are metastable (King *et al.*, 1977). Without exception, the voltage changes originating from the metastable levels were positive, indicating an ionization rate decrease, and the voltage changes originating from the nonmetastable levels were negative, indicating an ionization rate increase. In addition, the positive lines are stronger than the negative lines, indicating that electron impact ionization of metastables is the dominant ionization mechanism of the discharge.

The tuning mechanism of the dye laser

One of the purposes of these experiments was to test and calibrate the tuning mechanism of the dye laser. For this purpose, the spectra measured optogalvanically provided the necessary wavelength reference. Once the lines were identified, their wavelengths were readily available (Nestor, 1982). The linearity of the tuning mechanism of the dye laser could then be checked by plotting the known wavelengths versus their positions in units of stepper motor increments. Figure (8.4) below shows the results of this linearity check by giving the residual errors obtained with two different linear fits (left axis) and the average number of steps (stepper motor increments) per Ångstrom. The solid curve (open circles) gives the residual errors obtained after fitting to the ideal straight line. The ideal straight line passes through the first data point and has a slope of 50 steps per Ångstrom, as specified by the

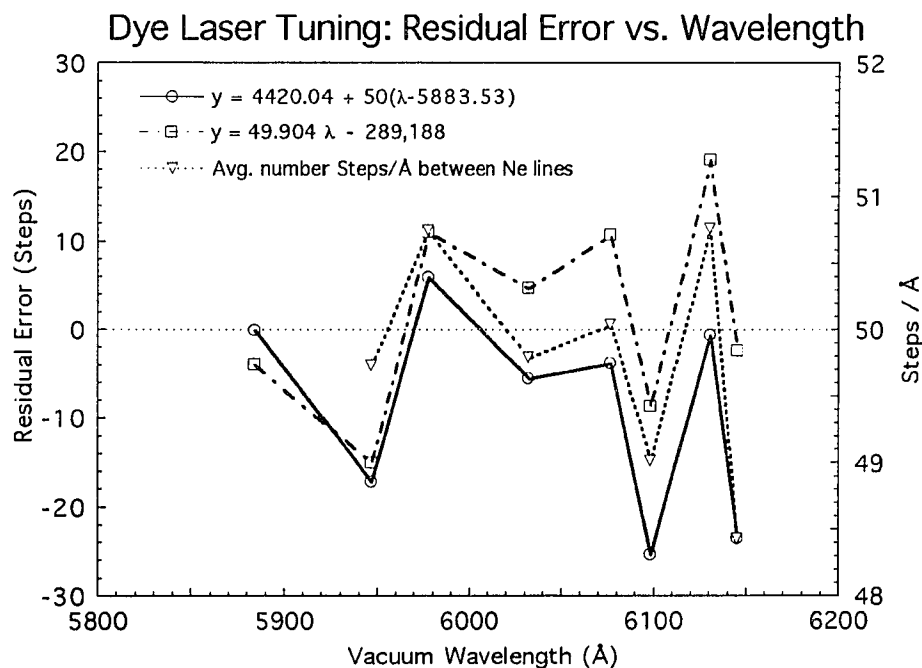


Figure (8.4)

manufacturer. The dot-dashed curve (open squares) shows the results of a

general linear fit in which the slope and intercept were allowed to vary.

Lastly, the average number of steps per Ångstrom obtained by dividing the difference in steps between adjacent lines by the difference in their wavelengths is presented (open triangles) which, in the ideal case, would be 50 for the entire data set. All curves give residual errors that, although small, are greater than might be expected from a consideration of the uncertainty in measuring the line positions. There are two explanations for this. Either the reference wavelengths used are incorrect, resulting in incorrect differences between adjacent lines, or the tuning mechanism of the dye laser is faulty.

There are two reasons why the reference wavelengths may be incorrect. Either the published values are wrong or the central wavelengths of the lines have been shifted due to collision induced processes (pressure shift) inside the discharge (Demtröder, 1981). Both these possibilities are highly unlikely. The pressure inside the Neon bulb used in these experiments was approximately 1 torr, resulting in a pressure shift of about 20 MHz. This corresponds to a shift of 2.5×10^{-4} Å, which is completely negligible. Therefore we are left with the possibility that the tuning mechanism of the dye laser is faulty. It is common to encounter backlash, or play between gears and/or pulleys in a mechanical system such as the tuning mechanism of the dye laser. However, in that case, a fit to the ideal straight line would give residual errors all of the same sign and these errors would presumably converge to zero during the scan. In addition, the overall average number of steps per Ångstrom would be greater than the "ideal" number of 50. Instead, the overall average obtained from the slope of the general linear fit is 49.94 ± 0.01 which indicates that the residual errors shown above are not due to backlash. The tendency of the residual errors shown above to oscillate about zero, or averages to oscillate about 50 steps/Å suggests that they come from a persistent, randomly oriented problem

with the mechanics of the tuning mechanism itself. This finding will be discussed further in the discussion of the experimental methods and procedures used for the LIF studies.

The Optogalvanic Line Shape and Laser Linewidth

We anticipated that the laser line shape could be obtained from a precise measurement of the optogalvanic spectrum of Ne in a low pressure discharge. The experimentally measured line shape is a convolution of the laser line shape and the absorption profile of the Ne line being investigated. The optogalvanically measured Neon lines are broadened by various mechanisms inside the discharge. In the limiting case, when the laser linewidth is much greater than the absorption profile, the linewidth can be read directly from the experimental data. However, this was not the case with the data presented here. In order to extract the laser linewidth from the present data, the various mechanisms that contribute to the broadening of the absorption profiles must be examined and quantitative estimates of their magnitudes must be obtained.

Broadening mechanisms fall into two classes: homogeneous, affecting all absorbing atoms equally, and inhomogeneous, affecting various subgroups of absorbing atoms differently. Homogeneous broadening mechanisms are described by a Lorentzian absorption profile; inhomogeneous broadening mechanisms, by a Gaussian profile. When both classes are present, the resulting line shape is a convolution of the individual Lorentzian and Gaussian profiles, which is called a Voigt profile (Demtröder, 1981). Examples of homogeneous broadening are natural broadening and pressure broadening. Inhomogeneous broadening is almost always due to Doppler broadening. Table (8.2) below lists the magnitudes of the various broadening mechanisms used to interpret the present data. A pressure of 1 torr and a temperature of 400 K (for

the atoms and ions) are assumed for the Neon bulb used in our experiments. From table (8.2) it is evident that Doppler broadening is by far the most important broadening mechanism. Therefore, the resulting absorption profile should be a Gaussian with a FWHM of approximately 0.02 Å.

Broadening Mechanisms	
Mechanism	magnitude (Å)
natural line width	1×10^{-4}
pressure broadening	2×10^{-3}
Doppler width	2×10^{-2}

Table (8.2)

Table (8.3) below lists the widths of all eight peaks detected and figure (8.5) shows two of the peaks, fitted to Lorentzians. Two points are evident: 1) all the lines have different widths, and 2) the lines are very well fitted by Lorentzians (*i.e.*, Gaussians provided a much poorer fit). From this it must be

Area and Width of the Optogalvanic Lines		
Wavelength (Å)	Area (counts)	Width (FWHM) (Å)
5881.90	5208	0.226
5944.83	11375	0.261
5975.53	4610	0.152
6030.00	358	0.156
6074.34	222	0.159
6096.16	240	0.164
6128.45	28	0.048
6143.06	947	0.088

Table (8.3)

concluded that, 1) homogeneous broadening is dominant, and 2) the laser linewidth cannot be read directly from the data. However, the experimentally measured line shapes can be explained very well by considering another

homogeneous broadening mechanism, not yet mentioned. Absorption profiles are broadened when the intensity of the incident radiation becomes high enough. This broadening mechanism is called saturation, or power broadening. Saturation broadening manifests itself as an increase in the total homogeneous width, and is expressed as

$$\gamma_S^2 = \gamma_0^2(1 + S_0), \quad (8.1)$$

where γ_0^2 is the total unsaturated homogeneous width (the total homogeneous width in the low power limit) and S_0 is the saturation parameter, given by

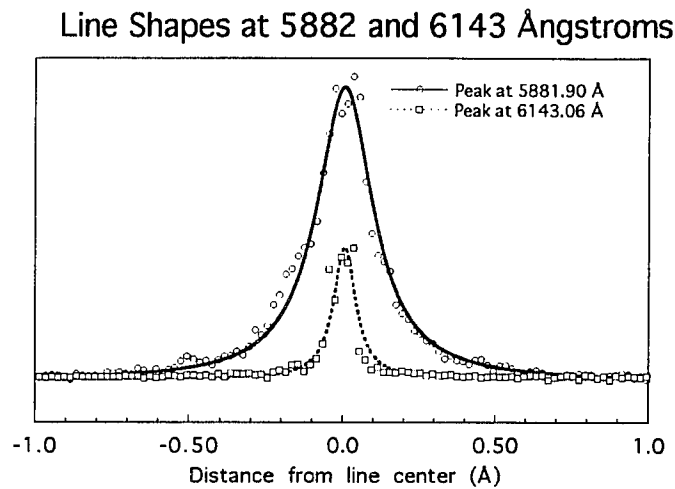


Figure (8.5)

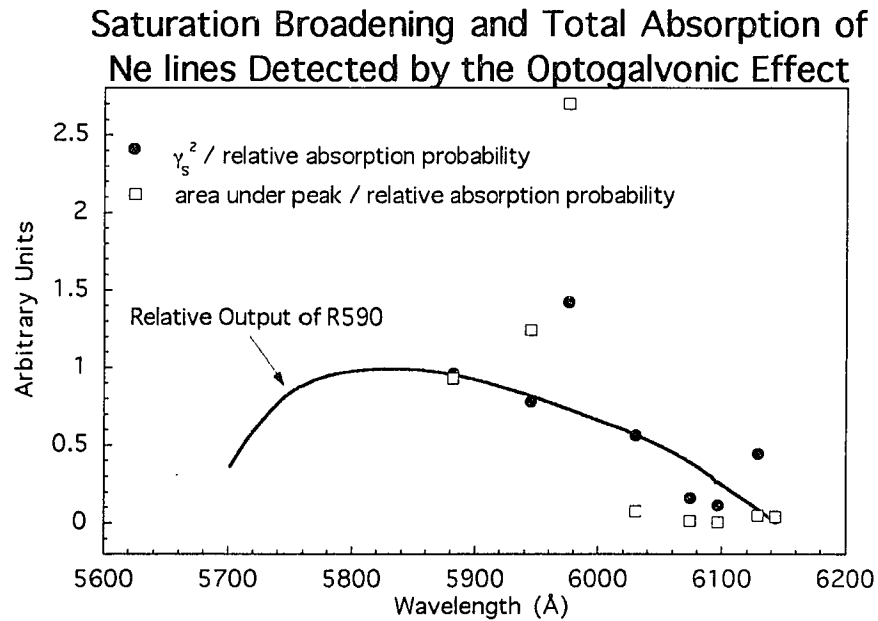
$B\rho/\mathfrak{R}$ where B is the absorption probability for the transition, ρ is the radiation density at the central wavelength, and $\mathfrak{R}$ is the mean relaxation rate for the two states involved in the transition being examined.

As previously stated, the experimentally measured line shape is a convolution of the laser line shape and the absorption profile. The absorption profile is itself a convolution of its homogeneously broadened and inhomogeneously broadened line shapes. To a first approximation, the experimentally measured linewidth is given by

$$\gamma_{\text{exp}}^2 = \gamma_{\text{H}}^2 + \gamma_{\text{D}}^2 + \gamma_{\text{las}}^2, \quad (8.2)$$

where γ_{H} is the total homogeneous width (with or without saturation), γ_{D} is the Doppler width, and γ_{las} is the laser linewidth. Using the linewidths listed in table (8.2) above and a laser linewidth between 0.02 and 0.03 Å, it is evident that, with the exception of the line at 6128.45 Å, equation (8.2) cannot account for the experimentally determined linewidths listed in table (8.3) above, without a consideration of power broadening.

The goodness of fit between the measured line shapes and the Lorentzian curves can be taken as evidence that the dominant broadening mechanism



must be power broadening of homogeneous absorption profiles. Additional evidence comes from figure (8.6) above, in which γ_{exp}^2/B is plotted against wavelength. Also included is the relative output power of the dye laser as obtained from a plot of the laser dye efficiency provided by the manufacturer of the R590 dye used in these experiments (Exciton Inc., 1992). When $S_0 \gg 1$, γ_{exp}^2/B should be proportional to ρ , the radiation density. It is remarkable that

the lines at 5944 Å and 6030 Å fall almost exactly on the curve of the relative output power ($< 4\%$ deviation). (Note that γ_{exp}^2/B and ρ have been normalized to each other at the peak at 5882 Å.) At the longest wavelengths, it is far from clear that the saturation parameter is much greater than one, so agreement is not expected. Also, the curve of the relative output power is likely to be highly inaccurate above 6030 Å, since the published curve had to be extrapolated to the longer wavelengths and different extrapolation methods yielded different results. However, the peak at 5975 Å has an anomalously large width which remains to be explained. Note that the intensity of this line as measured by the area under the peak is also anomalously large. There are two possible explanations for this anomaly. First, the absorption probability, taken from the CRC (Weast, 1980), may be in error. Although unlikely, this is the most straightforward explanation, explaining both the anomalously large area and width. Second, it has been reported (Keller *et al.*, 1980) that, although the intensities of spectral lines measured optogalvanically generally agree with the corresponding emission intensities measured spectroscopically, anomalies do occur. The intensity and shape of optogalvanic lines are determined by the dynamics of the discharge. As such they depend on the concentration of carrier gases (gases other than the one sustaining the discharge) present in the discharge bulb. Therefore, anomalies in the dynamics of the discharge, for example the collisionally induced relaxation rate, may result in an anomalously large intensity and/or width of an optogalvanic line.

Despite the anomaly at 5975 Å, it is clear that the widths of the peaks in the measured optogalvanic spectrum are explained remarkably well when saturation, or power broadening is taken into account. Therefore, it is reasonable to use the smallest measured linewidth, 0.048 Å as an upper limit for the unsaturated absorption linewidth of the Ne bulb. Using equation (8.1)

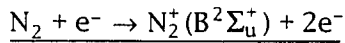
and neglecting all but Doppler broadening, we then get an upper limit of the laser linewidth $0.04 \text{ \AA}$, which compares favorably with the $0.02 \text{ \AA}$ to $0.03 \text{ \AA}$ linewidth reported by the manufacturer.

IX. Experimental Methods and Procedures

The present experiment is divided into two parts. The first part consists of the measurement of the electron impact produced $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+ (0,1)$ emission cross section. This measurement was performed using the optical method, described earlier in part I, "The Photoemission Experiment". This experiment involved only the gas beam and electron beam. The second part consists of the measurement of the cross section for the electron impact produced $N_2^+(X^2\Sigma_g^+)$ ground state ion. For this measurement, all three beams, gas beam, electron beam, and laser beam were employed. Since the pertinent features of the optical method have already been discussed, this chapter focuses on the second part of the present experiment; *i.e.*, the detection of ground state molecular and/or atomic fragments produced by electron impact using laser induced fluorescence (LIF).

The main principle underlying the effort to measure the cross section for producing $N_2^+(X^2\Sigma_g^+)$ by electron impact consists of measuring the absolute number density of $N_2^+(X^2\Sigma_g^+)$ by measuring its number density relative to the number density of $N_2^+(B^2\Sigma_u^+)$. Both species are produced simultaneously by electron impact under identical conditions. Therefore, the ratio of their number densities is proportional to the ratio of their respective cross sections. Since the cross section for electron impact produced $N_2^+(B^2\Sigma_u^+)$ is well known (Borst *et al.*, 1970), the cross section for the production of $N_2^+(X^2\Sigma_g^+)$ by electron impact can be deduced. In addition, since the cross section for production of $N_2^+(B^2\Sigma_u^+)$ is known, the measurements we obtained relating to $N_2^+(B^2\Sigma_u^+)$ production could be used as a diagnostic tool to check the proper operation of the apparatus. These data are presented first, followed by a discussion of the specific experimental techniques used to detect the presence of $N_2^+(X^2\Sigma_g^+)$ ground state ions.

Figure (7.2) shows a schematic diagram of the interaction region of the triple beam apparatus, showing the relative orientations of the three beams and the detection system. The electron beam and the laser beam are collinear with the laser entering the electron monochromator through a hole in the outer spherical sector. The inner surfaces of the electron monochromator are coated with Aerodag, which acts to reduce secondary electron emission, as well as to absorb scattered laser light, so that the electron monochromator, in addition to bending the electron beam, also serves as an optical baffle. The gas beam is perpendicular to the electron and laser beams and points downward. In order to maximize beam overlap, the long axis of the rectangular gas nozzle is parallel to the electron-laser beam axis and the nozzle is centered over the electron beam and laser beam. Lastly, the optical axis is perpendicular to the plane formed by the electron-laser beams and gas beam, such that the optical axis passes through the center of the interaction region.



The relative excitation function for the production of N_2^+ in its $B^2\Sigma_u^+$ excited state following electron impact was measured by monitoring the $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ (0,1) spontaneous emission as a function of impact energy. We used an interference filter with a 10 nm (FWHM) bandwidth instead of a monochromator to isolate the emission under study. Therefore, the measured signal from the monitored (0,1) band is a summation over all of the individual rotational lines populated by the electron impact process. The measured excitation function is therefore referred to as a band excitation function, and the signal is given by

$$S = \sigma(\bar{E})T \iint n_g(\bar{r})j_e(\bar{r})E(\bar{r})d\bar{r}, \quad (9.1)$$

where $\bar{E}$ is the mean kinetic energy of electrons in the electron beam, $\sigma(\bar{E})$ is

the $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ (0,1) band emission cross section, $n_g(\bar{r})$ is the target gas number density, $j_e(\bar{r})$ is the electron flux density, $E(\bar{r})$ is the detection efficiency of the optical collection system, T is the transmission of the interference filter multiplied by the quantum efficiency of the PMT, and the integration is over the entire volume, where the integrands have an appreciable value. This defines the interaction region.

Because the measured signal is a summation of the individual rotational lines of the (0,1) band, $\sigma(\bar{E})$, the band emission cross section in equation (9.1) above, is in reality the sum of excitation cross sections of individual rotational states of the N_2 targets. The sum is weighted by two factors. The first factor is given by the probability distribution of the initial rotational state population of the N_2 targets, assumed to be the usual Maxwell-Boltzmann distribution at room temperature. The second factor contains the line strengths of the individual R and P branch lines multiplied by the wavelength dependent part of the detection efficiency evaluated at the wavelength of the corresponding branch line. The second factor is given by $\frac{1}{2j+1} [S_{jk}^R T(\lambda_{jk}) + S_{jk'}^P T(\lambda_{jk'})]$ where j is the rotational quantum number of the excited ($B^2\Sigma_u^+$) state, S_{jk}^R and $S_{jk'}^P$ are the R and P branch line strengths, and $T(\lambda_{jk})$ and $T(\lambda_{jk'})$ are the detection efficiencies at the wavelengths λ_{jk} and $\lambda_{jk'}$. (The small difference in transmission probability of the R and P branch lines due to their wavelength difference has been ignored.) Because, as shown in figure (7.16) the wavelength dependent detection efficiency is essentially constant over the wavelength range of the (0,1) band, $T(\lambda_{jk})$ and $T(\lambda_{jk'})$ can be factored out of the sum. Next, because of the line strength sum rule (Herzberg, 1950), this sum subsequently reduces to 1, so that the overall factor written above reduces to T , as written in equation (9.1).

Shown in figure (9.1) below is the measured signal versus pushing

pressure, taken at an impact energy of 300 eV. This curve, analogous to figure (3.7) in part I, is used to normalize the data from different gases and different pushing pressures to each other. In addition, equation 9.1) can be used in conjunction with this curve to obtain an estimate of the target gas number

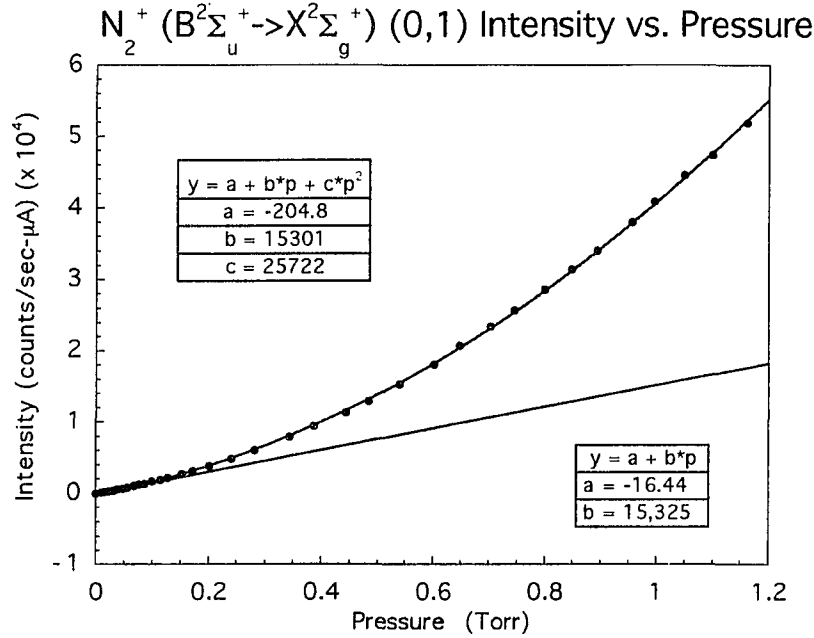


Figure (9.1)

density in the interaction region. Since the target gas number density and the detection efficiency of the optics are nearly constant over the cross sectional area of the electron beam, equation (9.1) can be integrated over this area to obtain

$$S = \sigma(\bar{E}) T I_{e^-} \int \bar{n}_g(\ell) \bar{E}(\ell) d\ell, \quad (9.2)$$

where I_{e^-} is the electron flux, $\bar{n}_g(\ell)$ and $\bar{E}(\ell)$ are averages over the electron beam cross section, and the integration is along the electron beam axis. Using the values calculated for the detection efficiency and the gas beam shape shown in figures (7.16) and (7.20), a value of 0.1 for the product of the filter transmission and the quantum efficiency of the PMT, and a value of $3.79 \times 10^{-18} \text{ cm}^2$ for the $N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+) (0,1)$ emission cross section at 300 eV impact

energy (Shaw *et al.*, 1983), it is estimated that the number density of N_2 molecules in the interaction region is $1.5 \times 10^{12}/\text{cm}^3$ per Torr of pushing pressure at low pushing pressures (≤ 0.1 Torr). This value is reasonable, based on experience, and lends credence to the values for the optical system detection efficiency calculated in the last chapter.

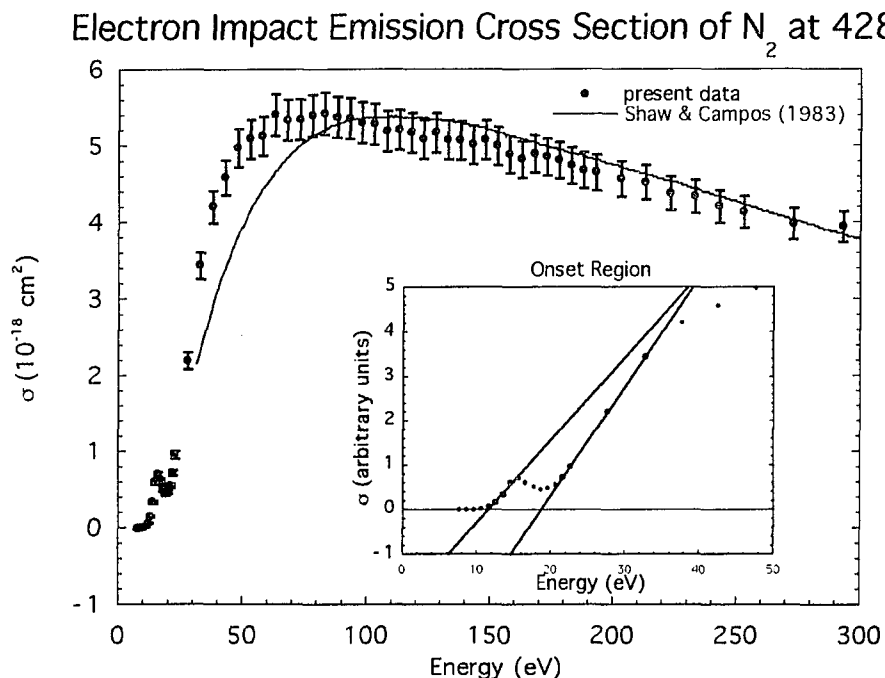


Figure (9.2)

Figure (9.2) above shows the measured cross section as a function of the electron impact energy. The expression obtained previously for the N_2 number density in the interaction region was used to normalize the relative cross section, so that the data points shown represent absolute emission cross sections. The error bars represent a 5% uncertainty based on an estimate of the fluctuations of the electron beam current. However, even after allowing for this uncertainty, there remains a slight discrepancy in the cross section shapes between the current data and that of (Shaw *et al.*, 1983), who measured the same emission cross section. The discrepancy might be due to the different

experimental conditions under which each experiment was performed.

Whereas Shaw *et al.*, (1983) used an optical monochromator with a resolution of 0.4 nm to select the $N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)(0,1)$ band, we used an interference filter with a relatively large bandwidth (10.5 nm) to select our emission. Table (9.1) below shows that several N_2 and N_2^+ bands fall within the bandpass region of the interference filter and therefore contribute to the measured emission (Pearse *et al.*, 1941). Because of its lower threshold energy,

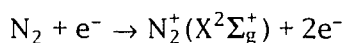
Band Systems Making up the Measured Emission Cross Section at 428 nm	
Emission	Bandhead (nm)
$N_2(C^3\Pi_u \rightarrow B^3\Pi_g)(1,5)$	427.0
$N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)(0,1)$	427.8
$N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)(1,2)$	423.6

Table (9.1)

the presence of the emission from the 2nd positive system of N_2 is evident from an examination of the onset region. Because the 2nd positive emission results from a singlet-triplet transmission, the cross section for its production decays rapidly at high energies (Stanton *et al.*, 1969). Therefore it is not expected to contribute much to the measured emission cross section above approximately 50 eV. On the other hand, the energy dependence of all the vibrational band cross sections of the 1st negative system of N_2^+ are expected to be very similar. The onset of the (1,2) band is about 0.3 eV higher than the onset of the (0,1) band, and its peak value is about 15% of the (0,1) peak value (Shaw *et al.*, 1983). Therefore, above approximately 50 eV, based on the emissions listed in table (9.1), our measured cross section should have the same shape, and should be about 15% larger than the $N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)(0,1)$ band emission cross section

measured by Shaw *et al.*, (1983). (Note that in figure (9.2) above, the (1,2) band was not included in the normalization.) In addition, there may be other, weak bands from the N_2 2nd positive system and the N_2^+ 1st negative system which contributed to the emission cross section we measured. Taking all of these factors into account, viz., the electron beam current fluctuations and the contaminating emissions from the 2nd positive system of N_2 and the 1st negative system of N_2^+ , the agreement between our cross section and the N_2^+ ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) (0,1) emission cross section measured by Shaw *et al.*, (1983) is satisfactory.

Lastly, we note that factors such as the presence of slow secondary electrons, reflected electrons, and the variation of the gas beam-electron beam overlap with electron impact energy can affect the measured cross section shape. The agreement between the shape of the emission cross section we measured and that of Shaw *et al.*, (1983) indicates that these factors did not significantly effect our measurements. We conclude that all components, not including the laser system, are functioning properly, *i.e.*, we have experimental conditions suitable for LIF detection.



As has been discussed, the bandwidth of the laser that is used to pump the $X^2\Sigma_g^+ \rightarrow B^2\Sigma_u^+$ (0,0) band is less than the spacing between individual rotational lines except very close to the bandhead. This implies that the excitation spectrum obtained by scanning the laser across the (0,0) band consists of individual rotational lines. Therefore, a necessary prerequisite to measuring the number density of N_2^+ in their $X^2\Sigma_g^+$ electronic ground states is to obtain a rotationally resolved excitation spectrum of $N_2^+(X^2\Sigma_g^+)$ (0,0).

Techniques for the effective use of the laser system

In order to allow the observation of an LIF signal, all of the parameters of the laser system have to be optimized, *i.e.*, the signal-to-noise ratio in the laser pulse, the pulse energy, the scattered laser light, and the precise control of the laser wavelength. This optimization required the development of specific experimental techniques and procedures that are discussed in the following paragraphs.

Two experimental conditions affecting the signal-to-noise ratio in the dye laser output have already been mentioned. The first one concerns the repetition rate of the excimer laser. It was found that the signal-to-noise ratio worsened steadily as the repetition rate of the excimer laser was increased above 40 Hz. This proved to be a bottleneck which limited the data acquisition rate. One possible solution to this problem is a redesign of the dye recirculation system. The second condition concerns the focus of the excimer laser beam into the dye laser cells. By monitoring the laser pulse energy output from the dye laser as the focus of the excimer laser into the amplifier cell of the dye laser was changed, we were able to maximize the signal-to-noise ratio in the dye laser output pulse.

Alignment of the dye laser beam through the vacuum chamber was crucial, as even a slightly misaligned laser could "blind" the PMT. (PMT blinding will be discussed shortly.) The laser pulse was steered into the vacuum chamber by a system of three mirrors and a variable number of apertures, typically three. Initially, the pulse output from the dye laser was vertically polarized, but because the mirror arrangement rotated the plane of polarization, the laser pulse entering the vacuum chamber was polarized horizontally. Examination

of the laser spot on a blank sheet of white paper as it emerges from the vacuum chamber is a very sensitive test of the laser alignment. Alignment was deemed acceptable when the paper displayed the laser spot as a set of concentric rings. These rings were caused by the diffraction of the laser passing through one or more of the apertures inside the vacuum chamber. It is even possible to (tentatively) determine which aperture inside the vacuum chamber is responsible for the diffraction by looking at the width of the rings. Thus, the symmetry of the diffraction pattern is a sensitive test of the quality of the alignment.

Lastly, perhaps the most critical aspect for the effective use of the laser system was the accurate and precise measurement of the dye laser wavelength. A SPEX model 500M Czerny-Turner spectrometer with a resolution of $0.2 \text{ \AA}$ was used for this purpose. A second PMT, located at the spectrometer exit slit, was used to monitor the output as the spectrometer was scanned by a built-in stepper motor. The wavelength of the dye laser measured with the spectrometer was reproducible from one measurement to the next to better than the measured linewidth. Figures (7.5) to (7.7) show several examples of the dye laser spectra. It should be noted that the spectrometer was calibrated using three lines ($3650.16 \text{ \AA}$, $3654.84 \text{ \AA}$, $3663.28 \text{ \AA}$) from a low pressure Hg discharge lamp. In order to eliminate the variation of the measured laser wavelength due to changes in the alignment of the laser into the spectrometer, the setup shown in figure (7.1) was used. Figure (7.1) shows that the laser is steered to the spectrometer entrance slit **after** it passes through the vacuum chamber. Assuming that the steering mirrors and spectrometer are fixed, the alignment of the laser into the spectrometer remains the same from one measurement to the next, thus eliminating variations of the alignment as a source of error in measuring the laser wavelength. When

measuring the laser pulse energy, the beam was intercepted by the energy meter, which also acted as a convenient beam stop.

The SR400 Gated Photon Counter

Because we used a continuous gas beam and electron beam, while the output of the laser system consisted of pulses of about 8 ns in duration, we employed gated detection to increase the signal-to-noise ratio. We used a Stanford Research model SR400 gated photon counter, which consists of an internal 200 MHz clock and three independent counting units containing an amplifier, discriminator, gate, and counter. The SR400 can be programmed to open a gate at a predetermined time after receiving a start pulse, or each gate can be held open continuously (CW). The trigger pulse can come from the internal clock or from an external source. The time between the trigger pulse and the opening of the gate, the gate delay, can be fixed or scanned. Additionally, the gate width can be fixed or scanned. The minimum gate width is 5 ns and the minimum gate delay is 25 ns. Lastly, each scanned parameter is programmed to increment after a predetermined number of trigger pulses, called the counting period, and a data point consists of the number of PMT pulses received during one counting period. In the present experiment, the SR400 was programmed to count trigger pulses which were obtained by directing a small portion of the dye laser output to a fast phototube (Hamamatsu model R1193U) that had a rise time of approximately 200 ps. In order to shape the output pulses of the phototube, they were first sent to a triggerable pulse generator (Datapulse model 101) before entering the SR400. The variation in the time between the peak of a phototube pulse and the SR400 trigger pulse was monitored with a Tektronix oscilloscope and found to be less than 20 ns. Since each laser pulse generates one trigger pulse, the rate of data acquisition

is determined by the repetition rate of the laser. The laser was typically run at 40 Hz and between 20 and 1000 laser pulses were accumulated per data point.

Photomultiplier tube blinding

Figure (9.3) below illustrates an effect of "PMT blinding". The expression "PMT blinding" comes from the fact that the PMT is temporarily unable to generate output pulses after a brief, intense burst of incident light which "overloads" the PMT. The two data sets in figure (9.3) were taken with an empty vacuum chamber and the incident laser power was varied by using neutral density filters. The "channel A" data were obtained using the SR400 with gate A open continuously (CW). Therefore, this data set gives the average count rate

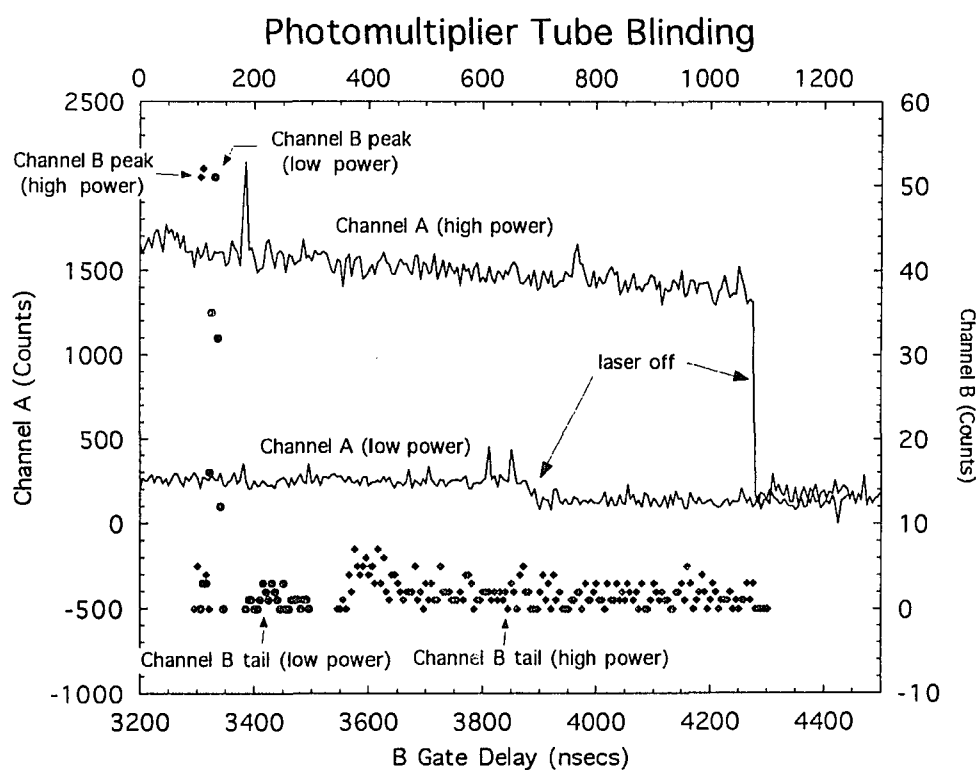


Figure (9.3)

per counting period (counts/5s) and it is proportional to the laser power. The top axis of figure (9.3) labels the elapsed time in seconds and show when the laser was turned off or blocked from entering the vacuum chamber. The difference between the two flat plateaus indicates the net PMT signal due to the laser, *i.e.*, the signal from dark counts, room lights, and possibly the electron gun filament is subtracted. We note that both data sets reach the same level, about 30 counts/s, after the laser is turned off. This signal is due to the dark count rate of the PMT plus the count rate from the room lights. The "channel B" data were obtained by programming the SR400 to open gate B for only 5 ns per laser pulse. In addition, the gate width was held fixed while the gate delay was incremented 5 ns after every 100 laser pulses. Therefore, the "channel B" data set represents the time-resolved laser pulse as seen by the PMT. The resolution, which is determined by the gate width, is 5 ns. For both "channel A" data sets, figure (9.3) shows two features separated by a period of time where no pulses were counted. This period of time, the "dead" time, is the origin of the term "PMT blinding". The first feature is a peak generated by the incident laser pulse. The second feature is a "tail" whose magnitude and position indicates how long the PMT was blinded. Figure (9.3) shows that a larger incident laser power blinds the PMT for a longer period of time (235 ns versus 45 ns). Also, the initial peak narrows (25 ns versus 45 ns) as the incident power increases. Note that the amplitudes of both peaks are identical, indicating that at this intensity, the PMT signal is not proportional to the incident flux. Figure (9.4) below compares two data sets, one that shows blinding and one that does not. (The data sets are displayed with a vertical offset for clarity of presentation.) In order to eliminate blinding, the incident laser power had to be decreased to between 5 and 50% of the maximum laser power depending on the experimental conditions. This indicates that the PMT

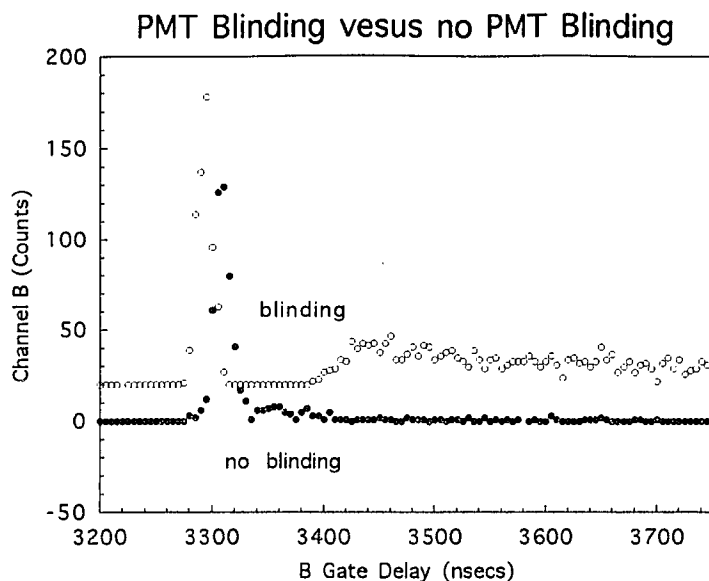


Figure (9.4)

is "saturated" by the high incident photon flux, and electrons leaving the photocathode of the PMT do not reach the anode.

Scattered laser light

The brief, intense pulse of light that causes PMT blinding described above originates from laser light scattered by any object inside the vacuum chamber. Note that the data shown in figures (9.3) and (9.4) were taken with the vacuum chamber empty, indicating that the PMT was blinded by laser light scattered from the entrance and exit windows. (Both entrance and exit windows were subsequently tilted to the Brewster angle and placed at the end of optical baffle arms that consisted of hollow pipes whose inner surface was coated with Aerodag.) Even when scattered laser light did not cause PMT blinding, it still obstructed the LIF signal. Therefore, it was essential to minimize the amount of scattered laser light reaching the PMT. In order to do this it was necessary to monitor the amount of scattered laser light per laser pulse reaching the PMT and the time required for the scattered laser light

signal to decay, so that experimental conditions that would ensure that these two parameters were always minimized could be maintained.

Figure (9.5) below shows the number of scattered laser light pulses received by the PMT versus the laser pulse energy (LPE). The data sets were taken with the Brewster angle windows, electron monochromator, Faraday cups, and gas beam nozzle in place, a pair of 427.8 nm central wavelength 4.0 nm bandpass (FWHM) interference filters in front of the PMT, and with the inner walls of the vacuum chamber coated with Aerodag. Laser pulse energies were measured with the Laser Probe energy meter situated behind the vacuum

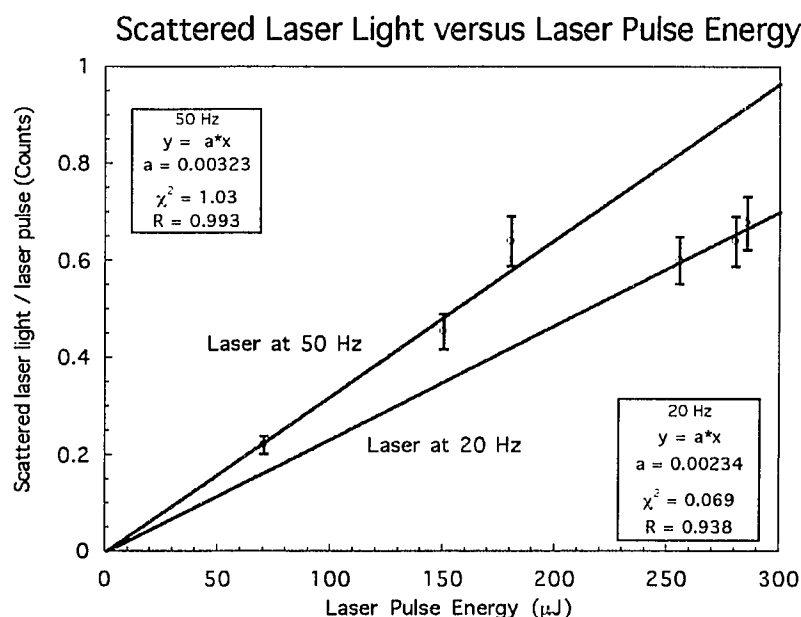


Figure (9.5)

chamber, ensuring an accurate measure of the laser pulse energy as it traversed the interaction region. Each data point represents an average of 1000 laser pulses. It was found that two different linear fits were necessary to describe the data for the laser run at two different repetition rates. As indicated earlier, the signal-to-noise ratio in a laser pulse decreased as the laser repetition rate increased. The decline started at a repetition rate between

30 and 40 Hz. The data in figure (9.5) indicate that the "noise" in the laser pulse contributes a disproportionate amount to the scattered laser light signal. This makes sense when one considers that the "noise" in the laser pulse comes from amplified spontaneous emission and laser dye fluorescence from the amplifier cell. Therefore, the "noise" has a higher divergence than the "signal" and will scatter more strongly from apertures. Note that both linear fits were constrained to pass through the origin and were thus limited to only one degree of freedom. An average of 0.0032 counts per laser pulse per μJ of laser pulse energy was obtained with the laser running at 50 Hz; the corresponding average for the laser running at 20 Hz was 0.0023. Both

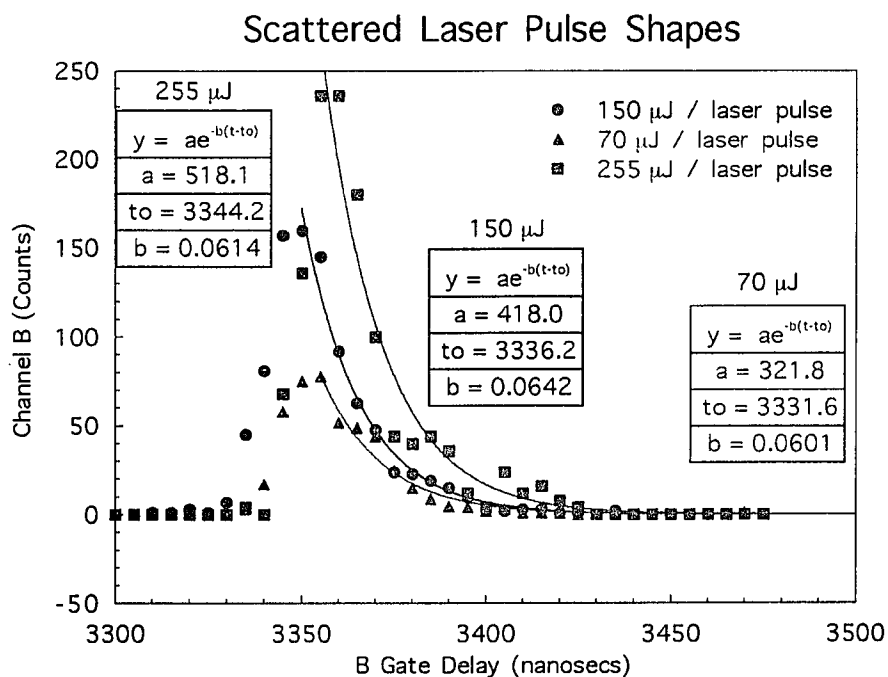


Figure (9.6)

numbers indicate that the observation of an LIF signal will not be hindered by the amount of scattered laser light reaching the PMT.

Shown above in figure (9.6) are the time resolved laser pulse shapes corresponding to the data in figure (9.5). A decaying exponential fit was

applied to each data set after the peak. These data sets indicate exactly when and how fast the scattered laser light pulse vanishes. All curves decay with a time constant of approximately 16 ns, which is consistent with the 20 ns rise and fall times of the PMT as specified by the manufacturer. This time constant determines the shortest excited state lifetime that can be measured with this apparatus. (Lifetimes shorter than this time constant can still be measured, but the resulting data will have to be deconvoluted to isolate the true lifetime.) Note that in all cases there is virtually no scattered laser light signal beyond 3.45 μ s after the trigger pulse. Therefore, in order to minimize the amount of scattered laser light contained in an LIF signal while allowing as much of the time dependent LIF signal as possible to be detected, this value was chosen for the gate delay of the SR400 photon counter.

Tuning the dye laser

The wavelength of the dye laser was measured *in situ* using the SPEX spectrometer described previously. The dye laser was tuned by revolving the tuning mirror about the center of the grating, as shown in figure (7.4). The position of the mirror can be read from a micrometer that is part of the tuning mechanism. The micrometer reading changes by 1/2 mil per Å of wavelength change. For precise wavelength tuning, the motion of the tuning mirror is controlled by a stepper motor, located near the oscillator on the laser platform. Sending pulses to the stepper motor revolves the mirror around the grating, which tunes the laser. According to the manufacturer, 500 pulses are required to change the wavelength by 1 Å which indicates that the minimum wavelength change is 0.002 Å, obtained for a single pulse. This minimum wavelength change is about 1/15 th the bandwidth of the laser, implying that when the laser is scanned across an absorption line which is much narrower

than the laser bandwidth, as in the present experiment, the signal of the absorption appears in only about 15 data points. This points to the **extreme** need for an accurate, precise and reproducible method of wavelength calibration. The SPEX spectrometer proved adequate, but the spectrometer calibration source, a low pressure Hg line lamp, and the dye laser had to be extremely well aligned into the spectrometer. In order to obtain the best resolution, the spectrometer entrance and exit slits were set to 10μ , the minimum slit widths possible. Light intensity was not a problem, and neutral density filters were used to attenuate the dye laser output when necessary. Figure (9.7) below shows the Hg lines used to calibrate the spectrometer. Note that the lines at 3662.88 and 3663.28 Å, though only 0.4 Å apart, are easily separated.

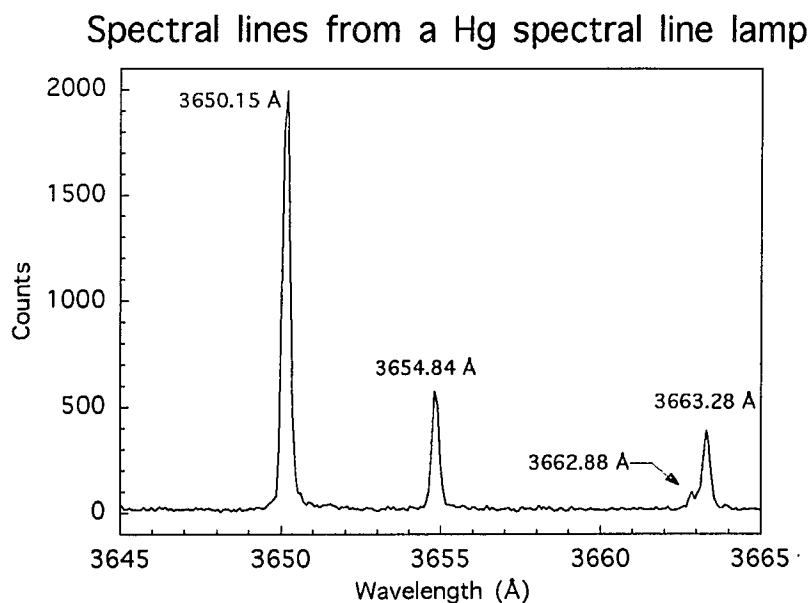


Figure (9.7)

The wavelength of the dye laser was measured before and after each attempt to detect the LIF signal from rotational lines of the $B^2\Sigma_u^+ \leftrightarrow X^2\Sigma_g^+ (0,0)$ band. A number of problems in the performance of the tuning mechanism of

the dye laser were encountered during the wavelength calibrations. First, two different kinds of mechanical "play" were found to be present. The first kind was slack between the pulleys connecting the stepper motor to the lead screw that pushed against the tuning mirror. The second kind was slack between the lead screw and the tuning mirror. The two different kinds of slack could be distinguished by the effect they had on the micrometer. When the lead screw turned; so did the micrometer, therefore, the first kind of slack was easily accounted for. However, the second kind proved more difficult. The stepper motor had to be sent pulses corresponding to a wavelength change of between 3 and 5 Å before the wavelength of the dye laser, as measured by the spectrometer, began to change. By monitoring the wavelength of the dye laser with the spectrometer at frequent intervals, this slack could also be accounted for. However, even after the "play" in the tuning mechanism was accounted for, there were still irregularities in the performance of the tuning mechanism. Figure (9.8) below shows the changes in the dye laser wavelength, as measured by the spectrometer, versus the wavelength increments sent to the dye laser in the form of pulses sent to the stepper motor, after both backlash sources had been cleared. Note that the straight line in figure (9.8) indicates perfect tuning. As shown, the micrometer tracked the stepper motor with reasonable accuracy, considering that the micrometer readings, which involved small changes, had to be made by visual inspection. (A magnifying glass aided in this procedure.) However, even after allowing for as much as a 0.1 Å uncertainty in the spectrometer reading, figure (9.8) shows that the tuning mechanism sometimes failed to increment by the proper amount. As a consequence, wavelength calibration had to be carried out at frequent intervals. When preparing to scan for an LIF signal, the wavelength of the dye laser was incremented by a small amount, followed

by a wavelength calibration, and this procedure was repeated until the wavelength was near enough to an $X^2\Sigma_g^+ \leftrightarrow B^2\Sigma_u^+$ (0,0) band rotational line to scan for an LIF signal. Clearly, a method is needed to monitor

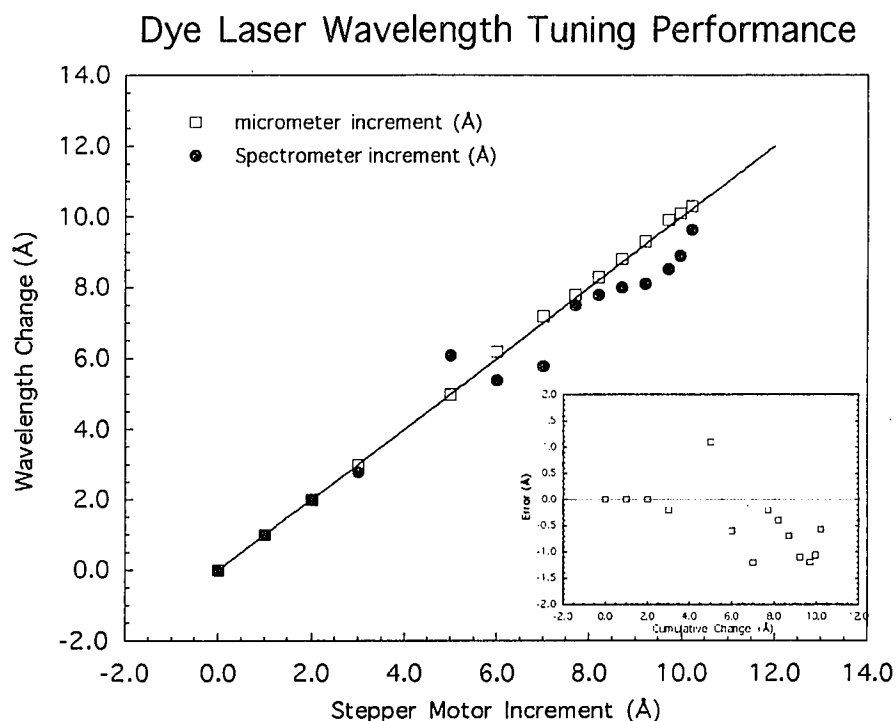


Figure (9.8)

the dye laser wavelength simultaneously while scanning for an LIF signal. Optogalvanic detection of a portion of the dye laser output might provide a solution to this problem. Using a commercial hollow cathode tube, Hippler *et al.*, (1993) have detected optogalvanic lines in the near ultraviolet, between 367 and 422 nm, and described an in-situ method for interpolating between the lines. Using this method, it should be possible to monitor the wavelength of the dye laser continuously, which would greatly decrease the need to rely on the reproducibility of the tuning mechanism of the dye laser.

Laser power required for saturation

The analysis of LIF data with the objective of extracting initial state populations depends heavily on the incident spectral energy density (photons/cm³-Hz) of the laser. Different results are obtained in the linear regime, where the number of molecules absorbing laser photons and subsequently spontaneously decaying depends linearly on the incident laser power and the fully saturated regime, where the observed fluorescence is completely independent of the incident laser power. Therefore, it is important to know how much laser power is required to cause saturation. The spectral energy density of a laser pulse depends greatly on its mode structure. In the current experiment, a single laser pulse typically consisted of 5 to 10 individual longitudinal modes whose separation was much greater than their width. This section describes a model used to estimate the spectral energy density of a single laser pulse from a measurement of the average total energy of a laser pulse.

Shown below in figure (9.9) is a typical laser pulse with its Gaussian envelope (FWHM approximately 0.2 cm⁻¹) obtained from an average of many pulses. Also shown are the individual longitudinal modes as seen in a single laser pulse. The separation between adjacent modes is approximately 0.02 cm⁻¹ and the FWHM of an individual mode is estimated to be 0.005 cm⁻¹ (Lumonics Inc., 1994 and Young, 1994). Small changes in the mode separation, the width of a mode, or the number of modes in the Gaussian envelope will not change the conclusions that follow. The single pulse mode pattern seen above is not reproducible on a pulse to pulse basis. This is mainly due to small fluctuations in the index of refraction of the laser dye solution which results in small changes in the optical path length. In addition, due to the statistics of the lasing process, the relative amplitudes of the various modes are also not

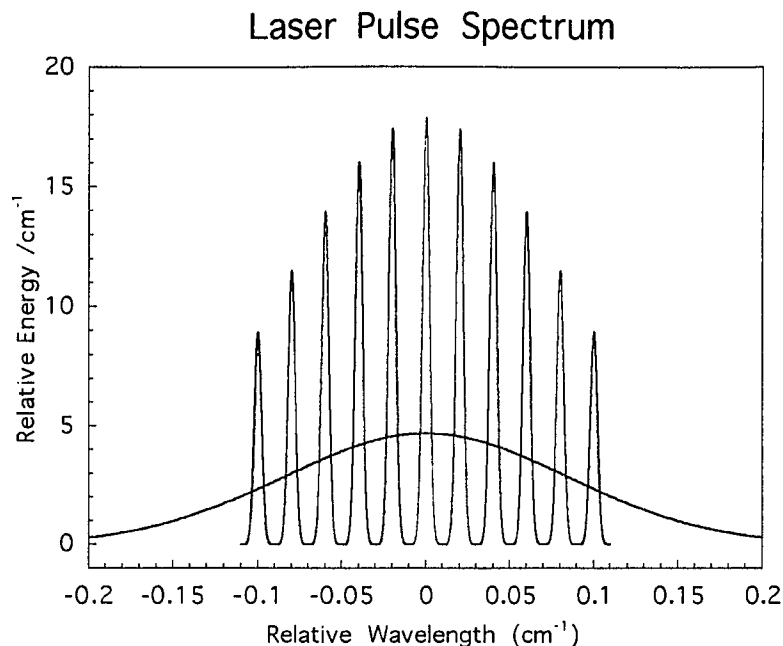


Figure (9.9)

repeated from one pulse to the next, and one or more modes may be absent from any given laser pulse.

It is clear from figure (9.9) that the spectral energy (energy/cm⁻¹ or energy/Hz) obtained after averaging over many pulses is much different, both in magnitude and distribution, than the spectral energy of a single pulse. Of course, the $N_2^+(X^2\Sigma_g^+)(v'', J'')$ molecular ions do not "see" an average laser pulse, but must absorb photons from a single pulse. Since the observed signal is a sum over many laser pulses, it represents the interaction of the $N_2^+(X^2\Sigma_g^+)(v'', J'')$ ions with a single pulse, averaged over many laser pulses. Note that because the time between laser pulses is extremely long (0.01 sec minimum) an individual N_2^+ ion has the opportunity to interact with only one laser pulse before it leaves the region where it can be detected.

An important question arises: what spectral energy does an $N_2^+(X^2\Sigma_g^+)(v'', J'')$ molecular ion actually experience, and with what probability? In order to investigate this question a calculation was made based on the following model.

Assume that

$$I(\lambda)d\lambda = \frac{E}{\sqrt{2\pi}\sigma} e^{-(\lambda-\bar{\lambda})^2/2\sigma^2} d\lambda \quad (9.3)$$

is the spectral energy distribution after pulse averaging, where E is the average energy/pulse, σ is the width of the Gaussian envelope ($\approx 0.2 \text{ cm}^{-1}$), and $\bar{\lambda}$ is the central wavelength of the envelope (*i.e.*, the wavelength set by the laser). The corresponding single pulse distribution is

$$f(\lambda)d\lambda = \sum_i \frac{a_i}{\sqrt{2\pi}\epsilon} e^{-(\lambda-\lambda_i)^2/2\epsilon^2} d\lambda, \quad (9.4)$$

where a_i gives the amplitude for the i^{th} mode, ϵ is the width of a single mode ($\approx 0.005 \text{ cm}^{-1}$), λ_i , the central wavelength of mode i , equals $i\delta$ where δ is the mode spacing ($\approx 0.02 \text{ cm}^{-1}$). We assume that $E = \sum_i a_i$, with no fluctuations in the mode amplitudes, and that $a_i \propto e^{-(\lambda-\lambda_i)^2/2\sigma^2}$ (*i.e.*, the mode amplitudes are distributed according to the average pulse shape). Now, λ is set to $\bar{\lambda}$, the central mode (corresponding to $i = 0$) is "jiggled" according to a Gaussian probability distribution with a FWHM of one half a mode spacing, and the probability distribution of the spectral energy experienced by an $N_2^+(X^2\Sigma_g^+)(v'', J'')$ ion is calculated. The resulting distribution, figure (9.10) clearly shows that an $N_2^+(X^2\Sigma_g^+)(v'', J'')$ ion experiences "all" or "nothing". A probability distribution of this type is expected when a narrow highly peaked function is varied over a wide range (*i.e.*, the mode width $\delta \gg$ the mode spacing ϵ). From looking at this probability distribution, it is clear that it does not make sense to talk about the average spectral energy an $N_2^+(X^2\Sigma_g^+)(v'', J'')$ ion experiences. Rather, the most probable spectral energies experienced are either 0 or $a_0/\sqrt{2\pi}\epsilon$. Using $\delta = 0.02 \text{ cm}^{-1}$, $\epsilon = 0.005 \text{ cm}^{-1}$ and 11 modes, $a_0/\sqrt{2\pi}\epsilon$ equals $17.88E/\text{cm}^{-1}$. This is approximately four times larger than the maximum spectral energy obtained using the average pulse shape and is likely

to be even larger, considering that the estimate used for the mode width ϵ , is conservatively large.

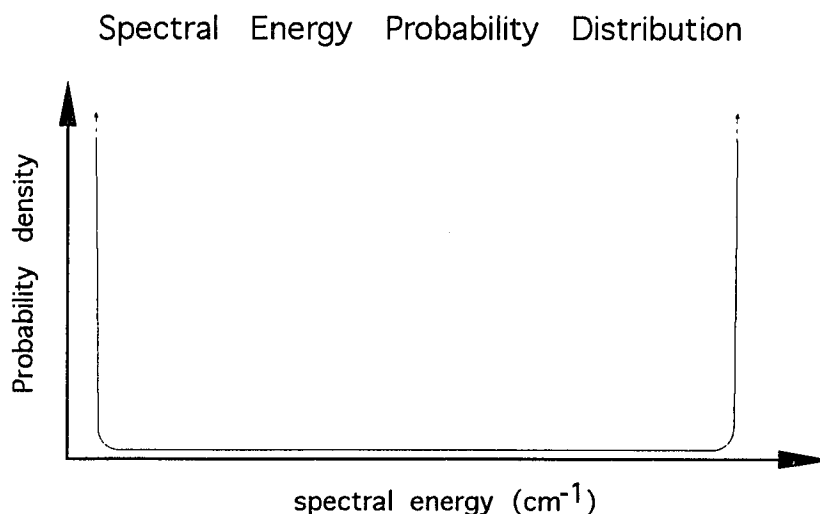


Figure (9.10)

Saturated absorption is explained as follows. The amount of absorption per laser pulse depends on two factors. The first is the maximum spectral energy per mode, $a_0 / \sqrt{2\pi} \epsilon$, and the second is the probability that an $N_2^+(X^2\Sigma_g^+)(v'', J'')$ experiences this spectral energy, which is given by the spectral energy probability distribution shown in figure (9.10). As the overall laser pulse energy is increased, the maximum spectral energy $a_0 / \sqrt{2\pi} \epsilon$ reaches the required value to cause saturation, at which point the amount of absorption cannot be increased further. Increasing the overall pulse energy beyond this point increases the number of photons/pulse but their spectral distribution remains unaltered; *i.e.*, the probability distribution shown in figure (9.10) remains unchanged. This implies that the amount of absorption, and therefore the amount of fluorescence per laser pulse, does not increase, and that the observed fluorescence is independent of the laser power. Using the specific parameters for the laser pulse above, the conclusion is that saturation occurs with roughly a factor of four times less laser pulse energy than

expected, based on a consideration only of an average laser pulse.

Estimated LIF Signal

Three factors determine the magnitude of the LIF signal. These are, the number density of N_2^+ ions in the initial state, $X^2\Sigma_g^+$ ($v=0, J$), the fraction of $N_2^+(X^2\Sigma_g^+)$ ($v=0, J$) ions pumped by the laser to the $B^2\Sigma_u^+$ ($v=0, J'$) excited state (*i.e.*, unsaturated or saturated absorption), and the fraction of laser pumped $N_2^+(B^2\Sigma_u^+)$ ($v=0, J'$) ions which decay back down to the $v = 1$ vibrational level of the $X^2\Sigma_g^+$ ground state. In addition, the LIF signal measured by the detector is obtained by an integration over the volume probed by the laser, analogous to equation (9.1), which pertained to the signal from electron-impact produced $N_2^+(B^2\Sigma_u^+)$.

First, the number density of N_2^+ ions in the $X^2\Sigma_g^+$ ground state is obtained through an equation that expresses the detailed balance between the rate at which $N_2^+(X^2\Sigma_g^+)$ are produced and the rate at which they are destroyed, analogous to equation (2.3). $N_2^+(X^2\Sigma_g^+)$ are produced directly through electron-impact and from electron-impact produced $N_2^+(B^2\Sigma_u^+)$ that decay back down to the $X^2\Sigma_g^+$ ground state, *i.e.*, there is a cascade contribution from the $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ process. Because ground state species do not decay, $N_2^+(X^2\Sigma_g^+)$ are "destroyed" only by leaving the region where they can be detected. Therefore, the number density of $N_2^+(X^2\Sigma_g^+)$ is given by the continuity equation,

$$\bar{v} \cdot \bar{\nabla} n_X(\bar{r}) = \sigma_{(X+B)} n_g j_e(\bar{r}) \quad (9.5)$$

where $\bar{v}$ is the velocity of an $N_2^+(X^2\Sigma_g^+)$ ion, n_X is the $N_2^+(X^2\Sigma_g^+)$ number density, $\sigma_{(X+B)}$ is the cross section for the direct production of $N_2^+(X^2\Sigma_g^+)$ via electron-impact plus the cross section for the cascade contribution from $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$, n_g is the number density of the N_2 target gas, and $j_e(\bar{r})$ is the electron flux density. In order to extract useful information from this equation, the

following approximations were made: 1.) n_g is constant throughout the region probed by the laser, and 2.) the only non-zero velocity component of the gas beam is v_z ; *i.e.*, the gas beam is perfectly collimated. With these approximations the solution to equation (9.5) can be written as

$$n_X(x, z) = \frac{n_g \sigma_{X+B}}{v_z} \int_{-\infty}^z j_{e^-}(x, z') dz' \quad (9.6)$$

where the x and z directions are defined in figure (7.2). Note that v_z is the Z -component of velocity of an $N_2^+(X^2\Sigma_g^+)$ ion, not an ensemble average. The average over the velocity distribution will be performed at the end. The integral in equation (9.6) above was computed assuming that the electron flux density is uniform over a circle of radius r_0 ; *i.e.*, $j_{e^-} = I_{e^-} / \pi r_0^2$. However the only quantity necessary to compute the LIF signal is the integral of $n_X(x, z)$ over the cross section of the laser beam. When the condition that the diameter of the laser beam in the interaction region is much larger than the diameter of the electron beam in the interaction region is fulfilled, this integral is relatively insensitive to the electron flux distribution. Using this distribution, the number of $N_2^+(X^2\Sigma_g^+)$ ions per unit length of the electron beam, $\int n_X(x, z) dx dz$, where the integration is over the cross sectional area of the laser beam, is given by $\frac{n_g \sigma_{X+B}}{v_z} \frac{2}{\pi} (R_0 + \frac{r_0}{3})$. Here R_0 is the radius of the laser

Values used to estimate the number of $N_2^+(X^2\Sigma_g^+)$ ions per unit electron beam length

n_g	$1.14 \times 10^{12} / \text{cm}^3$
σ_{X+B}	$70.5 \times 10^{-18} \text{ cm}^2$
I_{e^-}	$1.3 \times 10^{14} \text{ e}^- \text{ s} / \text{sec} (20.6 \mu\text{A})$
$\langle v_z^{-1} \rangle$	$2.7 \times 10^{-5} (\text{cm/sec})^{-1}$
R_0	0.15 cm
r_0	0.0125 cm

Table (9.2)

beam in the interaction region. Using the values in table (9.2) below, which have been calculated in the preceding paragraphs or measured in the present experiment, the result is $27,400 \text{ N}_2^+(X^2\Sigma_g^+) \text{ ions / cm of electron beam length}$. Note that $\langle v_z^{-1} \rangle$ is obtained by averaging v^{-1} over a Maxwell-Boltzmann distribution.

Next, in order to determine the fraction of $\text{N}_2^+(X^2\Sigma_g^+)$ ($v=0, J$) ions pumped by the laser to the $\text{B}^2\Sigma_u^+$ ($v=0, J'$) excited state, we need to calculate the $\text{B}^2\Sigma_u^+ \leftrightarrow X^2\Sigma_g^+$ (0,0) absorption probability, given by $B\rho(v_i)\Delta t_L$. In this expression B is the Einstein B coefficient for the $\text{N}_2^+(\text{B}^2\Sigma_u^+ \leftrightarrow X^2\Sigma_g^+)$ (0,0) transition, $\rho(v_i)$ is the incident spectral energy density, and Δt_L is the duration of a laser pulse. The electronic and vibrational part of the B coefficient, $\frac{8\pi^3}{3h^2} R_e^2(\bar{r}_{0,0}) q_{0,0}$, equals $6.92 \times 10^{25} / (\text{Joule}/\text{cm}^3\text{-Hz})\text{-sec}$ (Allen, 1963, and Lofthus et. al., 1977). ($R_e^2(\bar{r}_{0,0})$ is the square of electronic part of the electric dipole transition matrix element, evaluated at $\bar{r}_{0,0}$, the equilibrium internuclear distance for the (0,0) band, and $q_{0,0}$ is the (0,0) band Frank-Condon factor.) This expression must be multiplied by the line strength and the appropriate degeneracy factor. The degeneracy factor is $\frac{2}{2J''+1}$, where the 2 in the numerator comes from summing over the unresolved spin-doubled transitions and $2J''+1$ is the degeneracy of the initial state. Since the line strengths are either J'' (P branch) or $J''+1$ (R branch), this expression is approximately 1. Next we need the incident spectral radiation density, $\rho(v_i)$. Using the expression $17.88\text{E}/\text{cm}^{-1}$, obtained in the last section, $\rho(v_i)$ becomes $3.17 \times 10^{-10} \text{ E}/\text{cm}^3\text{-Hz}$, where E is the average pulse energy in Joules. Using 8 ns for the laser pulse duration, we obtain a value of $1.75 \times 10^8 \text{ E/s}$ for the absorption probability. With a laser pulse energy of 40 μJ , a value routinely obtained in the present experiment, we get an absorption probability of approximately 7020, a value well above the saturation threshold of 100 (see page 76). Therefore, we can safely use the expression $\frac{2J'+1}{(2J'+1)+(2J''+1)}$,

obtained previously in chapter VI, which applies under conditions of total saturation, for the fraction of $N_2^+(X^2\Sigma_g^+)$ ($v=0, J$) ions pumped by the laser to the $B^2\Sigma_u^+$ ($v=0, J'$) excited state.

Next, the fraction of laser pumped $N_2^+(B^2\Sigma_u^+)$ ($v=0, J'$) ions which decay back down to the $v = 1$ vibrational level of the $X^2\Sigma_g^+$ ground state is obtained by integrating the expression $A(0,1) e^{-t/\tau}$, giving the time dependence of the LIF signal (see equation (6.6)) with respect to time. The result is $A(0,1)\tau$ where $A(0,1)$ is the Einstein A coefficient for the $(0, -1)$ band of the $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ transition and τ is the lifetime of the $B^2\Sigma_u^+$ excited state. $A(0,1)\tau$ is called the branching ratio for decay from the $v'=0$ level of the $B^2\Sigma_u^+$ excited state to the $v''=0$ level of the $X^2\Sigma_g^+$ ground state. Lofthus et. al. (1977) give a value of $3.48 \times 10^6/s$ for $A(0,1)$ and a value of 62.5 ns for τ which gives a branching ratio of 0.22.

Finally, the equation which gives the LIF signal measured by the detection system is

$$S_{LIF} = TA(0,1)\tau \frac{2J'+1}{(2J'+1)+(2J''+1)} \frac{\sigma(\bar{E})_{X+B} I_{e^-}}{v_Z} \frac{2}{\pi} (R_o + \frac{r_o}{3}) \int \bar{n}_g(\ell) \bar{E}(\ell) d\ell \quad (9.7)$$

where all the quantities have been previously defined. Note that the integral appearing above is the same one that appears in equation (9.2), which gives the signal due to electron-impact produced N_2^+ in its $B^2\Sigma_u^+$ excited state. Therefore, this integral cancels when taking the ratio between the "excited state signal", given by equation (9.2) and the "ground state signal", given by equation (9.6). Also note that since this equation was derived using the approximations mentioned above, it is only approximate; i.e., the factor of $\frac{2}{\pi}$ appearing above depends on the model used for the electron flux distribution. However, it has the correct dependence on the following quantities: it predicts a larger LIF signal for the slower moving LIF targets (they are in the electron

beam for a longer period of time) and it predicts a larger signal LIF signal for a wide laser beam (more LIF targets are probed by the laser). In addition, since the LIF signal depends on the diameter of the laser beam in the interaction region, this diameter must be known in order to extract the absolute cross section for electron-impact produced $N_2^+(X^2\Sigma_g^+)$ from the ratio of the "excited state signal" to the "ground state signal" measured in the experiment.

Using the numbers given in the preceding paragraphs for the necessary quantities in equation (9.7) above, we obtain an estimate for the LIF signal measured by the detector of approximately 0.1 counts / laser pulse. This is to be compared with the signals measured concurrently with the LIF signal, namely the scattered laser light signal and the "excited state signal". The signal from scattered laser light was measured to be 0.0023 counts / μJ per laser pulse, which equals approximately 0.1 counts / laser pulse using a laser pulse energy of 50 μJ . However, using gated detection as previously discussed, at least 90% of this signal can be eliminated, rendering it negligible. On the other hand, the signal from the decay of electron-impact produced $N_2^+(B^2\Sigma_u^+)$ ($v=0$), the "excited state signal", which has been measured in the current setup is approximately 600,000 counts/s at the peak of the cross section. When this signal is measured using gated detection, as it is when scanning for an LIF signal, and using a gate width of 300 ns, the "excited state signal" is approximately 0.2 counts / laser pulse, and the only way to increase the ratio of "ground state signal" to "excited state signal" is to increase the number of LIF targets seen by the laser beam, *i.e.*, increase the laser beam diameter or modify the spatial overlap of the laser and electron beams by rearranging the mutual orientation of these two beams. It should be noted that the case of the electron-impact ionization of N_2 is not optimal because the $N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$

(0,0) photoemission cross section is large, *i.e.*, it is of comparable size to the cross section for the electron-impact production of $N_2^+(X^2\Sigma_g^+)$. In cases that are expected to be more typical, the measured photoemission cross section will be only a few percent of the cross section for the production of ground state species, so that the ratio of the "excited state signal" to the "ground state signal" will not be so poor. However, even though the ratio of "excited state signal" to "ground state signal", predicted above, is poor in the case of N_2^+ , the observation of an LIF signal should still be feasible using our current experimental setup. As will be shown in the next chapter, an LIF signal close to the value predicted above was, in fact, observed.

X. Results and Discussion

Results

Figure (10.1) below shows a plot of the time resolved LIF signal of electron impact produced $N_2^+(X^2\Sigma_g^+)$. The $X^2\Sigma_g^+(\nu=0) \rightarrow B^2\Sigma_u^+(\nu=0)$ band was pumped by the laser and the subsequent emission from the $B^2\Sigma_u^+(\nu=0) \rightarrow X^2\Sigma_g^+(\nu=1)$ band was monitored. The measured lifetime of 55 ± 10 ns is well within

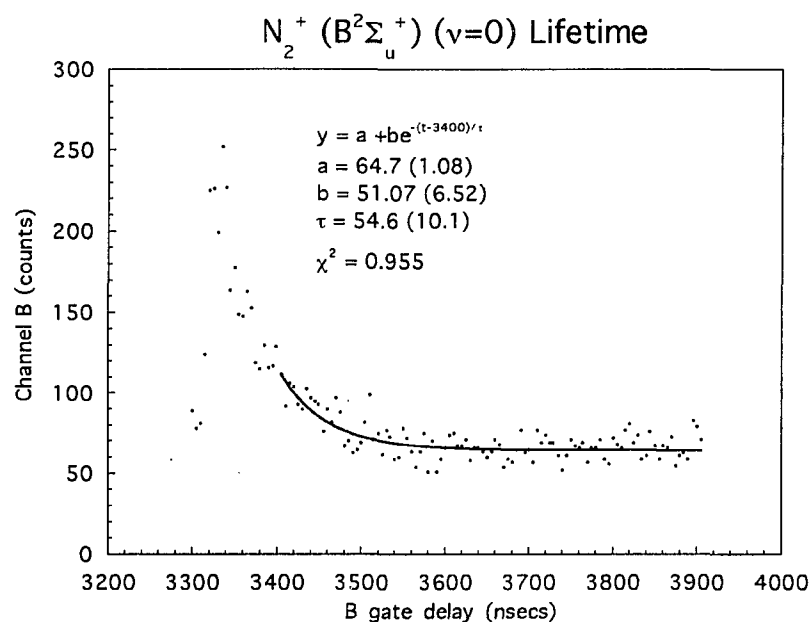


Figure (10.1)

the range of previous measurements (Lofthus *et al.*, 1977). Each data point represents the data accumulated over 5000 laser pulses. Only the portion of the curve after 3400 ns was used for the exponential fit to ensure that there was no contribution to the signal from scattered laser light. Note the flat background of approximately 64 counts which results from electron impact produced $N_2^+(B^2\Sigma_u^+)$. For this data set, the laser was run at 100 Hz, and the average pulse energy was approximately $45 \mu\text{ J}$. In addition, this data set was taken with the dye laser tuned past the tuning range of the dye, so that no lasing action was

occurring. Therefore, the signal shown above is due to the **noise** in the laser beam. Very similar data were obtained when the laser was tuned to other wavelengths chosen at random. This is consistent with other findings indicating the presence of a large amount of noise in the laser when it is run above 40 Hz. Figure (10.2) below shows similar data taken using Helium as the target gas. The measured lifetime is consistent with the value obtained for the decay of the scattered laser light signal (16 ns). (Note that for those data sets no gas or electron beam was used.) In addition, note the absence of the flat background signal which was present in figure (10.1). The conclusion is that figure (10.1) actually represents "LIF" from $N_2^+(X^2\Sigma_g^+)$ and is not an artifact of the apparatus.

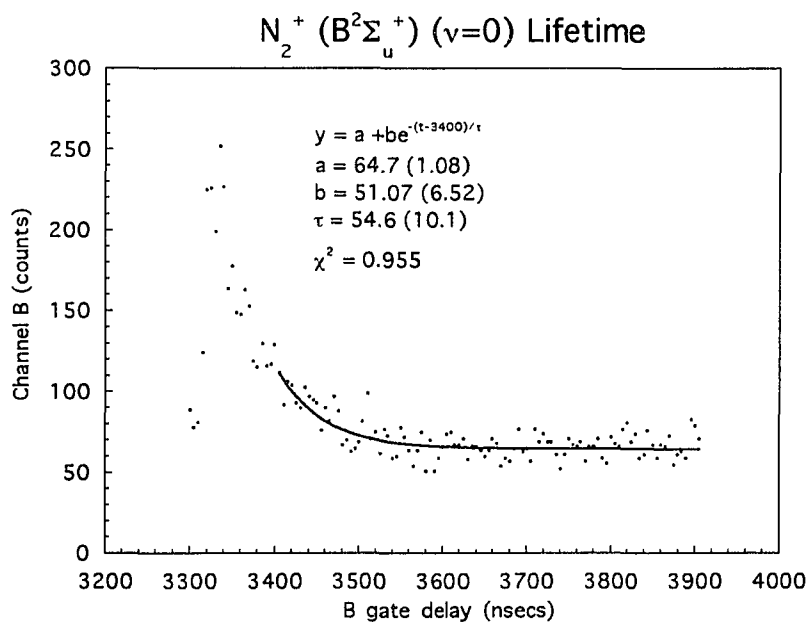


Figure (10.2)

Lastly, figure (10.3) below shows the only successful example of a wavelength-dependent LIF signal from $N_2^+(X^2\Sigma_g^+)$ obtained in this work. Even though the signal to noise ratio is very low, peaks can be seen in channel B. For this data set, gate B was set to open just after the end of the laser pulse,

appropriately adjusted to avoid the scattered laser light signal, and was kept open for 600 ns (≈ 10 lifetimes). Gate A was set to open when the gate B closed, and was also open for 600 ns. For this data set, the repetition rate of the laser

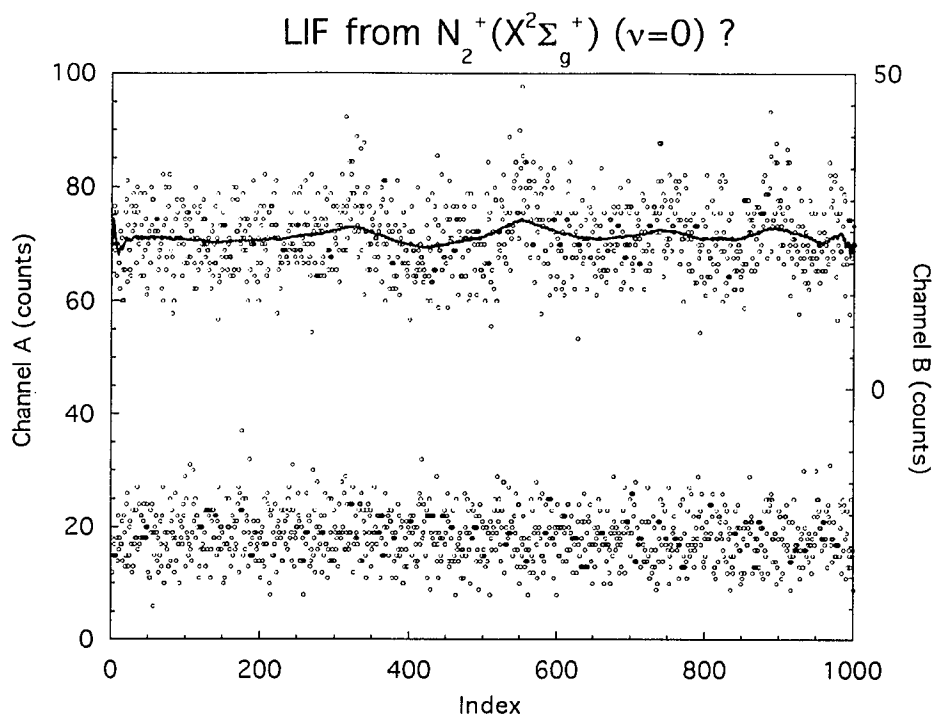


Figure (10.3)

was 40 Hz, and the laser pulse energy was approximately $35 \mu\text{ J}$. Since the laser was being scanned towards longer wavelengths, and was close to the bandhead in the P branch, the peaks are tentatively labeled P(8) through P(11), however the signal to noise ratio is too poor to make a definite assignment.

Discussion

There are theoretical and experimental reasons why we were not successful in observing a wavelength-dependent LIF signal from $N_2^+(X^2\Sigma_g^+)$. The most likely reasons are experimental. The single most important reason concerns the wavelength tuning of the dye laser. It has been demonstrated that the wavelength of the dye laser could not be incremented as precisely and

reliably as required for this experiment. It is likely that wavelength scans were made where, in actuality, the wavelength of the laser did not change at all. The rate of data acquisition for this experiment was slow. It took up to 6 hours to scan the laser 4 Å. The conclusion is that a more precise wavelength calibration method and a better ability to increment the wavelength of the dye laser in a reproducible way are essential to the success of this experiment.

As evidenced in figure (10.1), there was, at times, enough intensity in the noise of a laser pulse to pump ground state N_2^+ . This noise created a wavelength-independent background that reduced the maximum observable wavelength-dependent LIF signal. The worst case scenario would be total saturation of the $X^2\Sigma_g^+ \rightarrow B^2\Sigma_u^+$ (0,0) band by the noise in the laser pulse. In that case, no wavelength-dependent LIF signal would be possible at all. While the signal-to-noise ratio was dramatically improved through proper excimer beam focusing and alignment, and acceptable values were achieved, close attention must be paid constantly to this experimental parameter.

The next issue is beam overlap, specifically the spatial overlap of the gas, electron, and laser beams. If the electron beam is not properly focused, there will be a region outside the region probed by the laser producing an emission that is detected with the same efficiency as the LIF signal. Fluctuations in the electron beam current act as a source of noise when scanning for a wavelength dependent LIF signal. An electron beam which is not properly focused increases the fluctuations in the electron beam-gas beam signal but does not affect the LIF signal at all. The result is a decreased signal-to-noise ratio. The diameter of the electron beam increased after the apertures in the electron monochromator were removed, as evidenced by the smaller ratio of currents measured in the inner and outer Faraday cups. If possible, it is desirable to ensure that, in the interaction region, the laser beam is wider

than the electron beam.

Lastly, it should be noted that only LIF signals originating from the $v=0$ level of $N_2^+(X^2\Sigma_g^+)$ were searched for. According to the Frank-Condon factors for ionization, the $v=0$ level should be by far the most heavily populated ($q_{0,0}/q_{0,1}$ is approximately 10). Though not likely, it is possible that the ionization of $N_2(X^1\Sigma_g^+)$, forming $N_2^+(X^2\Sigma_g^+)$, is not a process governed by the Frank-Condon principle. As discussed, it has been proposed that the ionization of $N_2(X^1\Sigma_g^+)$, forming $N_2^+(X^2\Sigma_g^+)$, occurs via the creation of an excited state complex consisting of an $N_2^+(X^2\Sigma_g^+)$ ionic core and an electron in a Rydberg state that subsequently "autoionizes", leaving the $N_2^+(X^2\Sigma_g^+)$ ion (Zetner *et al.*, 1988). In such a process, the Frank-Condon principle is likely to be violated. There is experimental evidence of this possibility. In a series of recent experiments involving the charge exchange of N_2 in collisions with either Ar^+ or N_2^+ , (Frost *et al.*, 1993) have observed vibrational heating in the N_2^+ product under certain conditions. Only a successful measurement of the electron impact ionization cross section to the various vibrational levels of the ground state N_2^+ ion will conclusively answer this question.

XI. Conclusions and Suggestions for Further Research

The Photoemission Experiment

Electron-impact induced dissociative excitation of the simple halogen containing molecules SF_6 , CF_4 , NF_3 , CCl_2F_2 , and BCl_3 was studied by 1) identifying the prominent emission features following electron impact by performing spectral surveys, and 2) by measuring the absolute photoemission cross sections for these emissions. These molecules were chosen because of their widespread use as the feedstock molecules for low temperature processing plasmas. Complete spectral surveys of these molecules, between approximately 80 and 800 nm, were performed, in some cases for the first time. Threshold energies for the various emissions along with the shapes of the photoemission cross sections were used to determine the dissociation channels leading to the emitting fragment being studied. Not surprisingly, atomic fluorine emissions dominated the fluorine containing molecules. For the molecules SF_6 , CF_4 , and NF_3 , total fragmentation was found to be the dominant dissociation mechanism leading to the production of an excited fluorine atom. The molecule CCl_2F_2 was slightly more complicated; *i.e.*, partial fragmentation was found to be responsible for some emissions while total fragmentation was responsible for others. Cascade from higher excited states of atomic fluorine was found to contribute significantly to the apparent emission cross sections in the VUV.

In the case of BCl_3 , emission lines from atomic boron and vibrational band emissions from BCl were detected. For the boron line and BCl vibrational band photoemission cross sections measured, a double onset structure was found, with the second onset higher than the first by approximately the ionization energy of atomic chlorine. This indicates that both dissociation mechanisms, the one leading to the production of excited boron atoms and the one leading to

the production of excited BCl molecules, are themselves composed of two different dissociation mechanisms, a "neutral" channel which produces a ground state chlorine atom, and an "ionic" channel which produces a ground state chlorine ion.

The "Triple-Beam" experiment

A new experiment, called the "triple-beam" experiment, for the study of electron-impact processes in which the products are left in their ground states, was designed and a new apparatus for this experiment was built. The "triple-beam" experiment was designed to measure cross sections for the production of electron-impact fragments left in their ground states by using LIF to measure the population densities of ground state products. The first reaction studied was the electron-impact ionization of N_2 ; *i.e.*, $N_2 + e^- \rightarrow N_2^+(X^2\Sigma_g^+) + 2e^-$, where it was desired to measure the number density of the electron-impact produced $N_2^+(X^2\Sigma_g^+)$ ground state ion. Preliminary data were obtained which used time resolved LIF to measure the lifetime of the $N_2^+(B^2\Sigma_u^+)$ excited state. The main impediment to further progress concerns the precise control of the wavelength of the dye laser. Because the dye laser wavelength could not be set reliably enough, a way to monitor the wavelength *in-situ* on a continuous basis is necessary. As discussed in the text, optogalvanic detection of a portion of the dye laser output pulse may provide a solution to this problem.

The application of LIF to the measurement of electron-impact produced ground state species using an effusive gas beam and a continuous electron beam is technically challenging because of the weakness of the signals involved. Overall signal strengths and signal-to noise-ratios sufficient to allow the observation of an LIF signal were obtained; however, the ever-

present challenge is to further increase these experimental parameters in order to allow LIF detection to be made under less than optimal conditions and to allow trade-offs to be made for special circumstances. The most feasible way to increase the overall signal strength is to increase the electron beam current. However, because the LIF technique measures densities, in order for it to increase the overall signal strength, the electron beam current needs to be increased without increasing the beam diameter in the interaction region. This may require adding focusing elements to the electron beam system. In addition, since the LIF signal decays exponentially beginning at the end of the laser pulse, the closer in time to the end of the laser pulse we probe for ground state N_2^+ ions the larger our LIF signal will be. The factor which limits how close in time to the end of the laser pulse we can probe is the amount of scattered laser light that reaches the detector. It is therefore desirable to continue to decrease the amount of scattered laser light reaching the detector. This may be possible by modifying the size, shape, and location of the aperture inside the vacuum chamber which limits the photon detector viewing angle.

There are several ways to improve the signal-to-noise ratio of the signals obtained in the triple-beam experiment. A wavelength independent LIF signal attributable to noise in the laser output pulse points to the need to improve the signal-to-noise ratio in the laser output pulse. Two ways to accomplish this are to incorporate a polarizing element (*i.e.*, a Glan prism) and/or a spatial filter between the dye laser and the vacuum chamber. (Since the signal in the laser output pulse is polarized while the noise is not, using a polarizer with its transmission axis parallel to the polarization axis of the signal will decrease the noise by a factor of two.) The drawback to using a spatial filter is the overall loss of laser pulse energy. In the case of N_2^+ , the loss of laser pulse energy should not prevent the saturation of the $B^2\Sigma_u^+ \leftrightarrow X^2\Sigma_g^+$ transition, but

this may not be true for other molecules.

The above suggestions for increasing the ease by which the LIF signal is detected do not require a fundamental modification of the "triple-beam" apparatus. Using a pulsed electron beam requires fundamental changes to the apparatus, but has an advantage that is worth consideration. Essentially, the use of a pulsed electron beam eliminates the need to detect fluorescence originating from the $B^2\Sigma_u^+$ excited state and $X^2\Sigma_g^+$ ground state simultaneously. This would eliminate the noise in the LIF signal caused by unavoidable fluctuations in the electron beam current. (Fluctuations in the electron beam current cause fluctuations in the fluorescence from electron-impact produced $N_2^+(B^2\Sigma_u^+)$ ions, which act as a source of noise in the detection of an LIF signal from $N_2^+(X^2\Sigma_g^+)$.) The drawback to using a pulsed electron beam is that the population probed by the laser under these circumstances is the sum of N_2^+ created in its $X^2\Sigma_g^+$ ground state and $B^2\Sigma_u^+$ excited state. This entails an additional measurement in order to isolate the population of N_2^+ created in its $X^2\Sigma_g^+$ ground state that is not necessary when detecting both populations simultaneously.

Lastly, we come to possibilities for future research that have to do with interesting physics. The narrow bandwidth of the laser implies that the cross sections obtained using LIF are the cross sections for the production of one individual rotational state of the electron-impact-created final product, and it is therefore possible, in principle, to measure all of them. This opens up the possibility of detecting trends and anomalies in these cross sections which could provide detailed information about the dynamics of the electron-impact process which created the product. An example that bears on the electron-impact ionization of N_2 has already been mentioned; *i.e.*, the possibility that the Frank-Condon principle is violated during the production of N_2^+ in its

$X^2\Sigma_g^+$ ground state. A violation of the Frank-Condon principle in this circumstance would be positive evidence for the existence of the excited state complex proposed as the parent of $N_2^+(X^2\Sigma_g^+)$. On the other hand, the sum of all the cross sections for the production of individual rotational states in a single vibrational band can be used to measure Frank-Condon factors when they are not known. Perhaps even more exciting is the possibility of detecting a net change in the rotational temperature between parent and product which cannot be accounted for by a line strength based on an electric dipole transition. Again, this bears on the electron-impact ionization of N_2 where, using a supersonic gas beam, exactly this phenomenon has been reported for the production of N_2^+ in its $X^2\Sigma_g^+$ ground state (Zetner *et al.*, 1988).

Of course, using target molecules more exotic than N_2 , where the electron-impact ionization and/or dissociation cross sections are not known, increases the possibility of seeing interesting physics, e.g. the halogen containing molecules NF_3 , CF_4 , SF_6 , CCl_2F_2 , and BCl_3 , which were discussed in the Part I of this work. With this in mind, the use of frequency doubling techniques to increase the wavelength range of the laser system greatly increases the number of transitions that can be pumped and therefore the number of molecules that can be studied. Lastly, measuring dissociation cross sections involves the challenge that fragments may be produced with enough excess kinetic energy so that they leave the viewing region before they can be detected. However, along with this challenge is the possibility of measuring this kinetic energy by using a pulsed electron beam and monitoring the variation of the LIF intensity as the time between the electron beam pulse and the laser pulse is varied. This would allow the measurement of the location and shape of the potential energy surfaces involved in the production of the fragment being studied.

In conclusion, the use of LIF to measure the population densities of ground state products created by electron-impact is a very powerful technique that is applicable to a wide range of processes. Because of its wide range of applicability, it is worth overcoming the technical obstacles required for its development.

Bibliography

- Aarts, J. F. M., "Ion and Electron Impact Ionisation of CF_4 Studied Via UV Emission," *Chemical Physics Letters* **114** (1), 114-120 (1985).
- Aarts, J. F. M. and F. J. De Heer, "Emission Cross Sections for NI and NII Multiplets and some Molecular Bands for Electron Impact on N_2 ," *Physica* **52**, 45-73 (1971).
- Ajello, J. M., D. E. Shemansky, B. Franklin, J. Watkins, S. Srivastava, G. K. James, W. T. Simms, C. W. Hord, W. Pryor, W. McClintock, V. Argabright, and D. Hall, "Simple ultraviolet calibration source with reference spectra and its use with the Galileo orbiter ultraviolet spectrometer," *Applied Optics* **27** (5), 890-914 (1988).
- Ajello, J. M., D. E. Shemansky, T. L. Kwok, and Y. L. Yung, "Studies of extreme-ultraviolet emission from Rydberg series of H_2 by electron impact," *Physical Review A* **29** (2), 636-653 (1984).
- Ajello, J. M., S. Srivastava, and Y. L. Yung, "Laboratory studies of uv emissions of H_2 by electron impact, The Werner- and Lyman-band systems," *Physical Review A* **25** (5), 2485-2498 (1982).
- Allen, C. W., *Astrophysical Quantities* (University of London, Athlone Press, London, 1963).
- Allison, A. C. and A. Dalgarno, "Band Oscillator Strengths and Transition Probabilities for the Lyman and Werner Systems of H_2 , HD, and D_2 ," *Atomic Data* **1**, 289-304 (1970).
- Allison, J., T. Kondow, and R. N. Zare, "Laser-Induced Fluorescence Measurement of the Nascent Rotational Distribution of $\text{N}_2^+(\text{X}^2\Sigma_g^+)$ Formed by Electron Impact on N_2 ," *Chemical Physics Letters* **64** (2), 202-204 (1979).
- Altkorn, R. and R. N. Zare, "Effects of Saturation on Laser-Induced Fluorescence Measurements of Population and Polarization," *Annual Review of Physics and Chemistry* **35**, 265-289 (1984).
- Ashcroft, N. W. and N. D. Mermin, *Solid State Physics*, 1st ed. (Holt, Rinehart and Winston, Philadelphia, 1976).
- Bashkin, S. and J. O. Stoner Jr., *Atomic Energy Levels and Grotrian Diagrams* (North-Holland Publishing Company, Amsterdam, 1975).
- Becker, K. H., "Electron-Impact Ionization and Dissociative Excitation of Halogen-Containing Molecules," *Comments on Atomic and Molecular Physics* **30** (5), 261-284 (1994).
- Becker, K. H., B. Stumpf, and G. Schulz, "Polarisation of the $\text{OH}(\text{A}^2\Sigma^+, v'=0 \rightarrow \text{X})$

$^2\Pi_{1/2}, v''=0$) Fluorescence Produced by Electron Impact on Water Vapour," *Chemical Physics* **53**, 31-38 (1980).

Berkowitz, J., *Photoabsorption, Photoionization, and Photoelectron Spectroscopy* (Academic Press, New York, 1979).

Blanks, K. A. and K. Becker, "Optical emissions in the wavelength region 2000-6000 Å produced by electron impact dissociation of NF_3 , CF_4 and SF_6 ," *Journal of Physics B: Atomic and Molecular Physics* **20**, 6157-6163 (1987a).

Blanks, K. A., A. E. Tabor, and K. Becker, "Absolute cross sections for fluorine $3p \rightarrow 3s$ line emissions following single electron impact on NF_3 , CF_4 , SF_6 ," *Journal of Chemical Physics* **86**, 4871-4875 (1987b).

Borst, W. L. and E. C. Zipf, "Cross Section for Electron-Impact Excitation of the (0,0) First Negative Band of N_2^+ from Threshold to 3 keV," *Physical Review A* **1**, 834-840 (1970).

Bouchoux, A. M., R. Bacis, J. P. Gouere, and A. M. Lambert, "Relative Intensities of the Rotational Lines of the (0,0) and (0,1) Bands of the $\text{B}^2\Sigma^- - \text{X}^2\Sigma$ Systems of N_2^+ ," *Journal of Quantitative Spectroscopy and Radiation Transfer* **16**, 451-456 (1976).

Brion, C. E. and A. Hamnett, "Continuum Optical Strength Measurements By Electron Spectroscopy in the Gas Phase," in *The Excited State in Chemical Physics*, edited by J. W. McGowan (John Wiley and Sons, New York, 1981), Vol. XLV, pp. 1-80.

Bruce, M. R., C. Ma, and R. A. Bonham, "Positive Ion Pair Production by Electron Impact Dissociative Ionization of CF_4 ," *Chemical Physics Letters* **190**, 285-290 (1992).

Case, D. A., G. M. McClelland, and D. R. Herschbach, "Angular momentum polarization in molecular collisions: Classical and quantum theory for measurements using resonance fluorescence," *Molecular Physics* **35** (2), 541-573 (1978).

Chase Jr., M. W., C. A. Davies, J. R. Downey Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, "JANAF Thermochemical Tables (Third Edition)," *Journal of Physical and Chemical Reference Data* **14** (Supplement No. 1) (1985).

Clout, P. N. and D. W. O. Heddle, "Elimination of Polarization Corrections from Optical Excitation-Function Measurements," *Journal of the Optical Society of America* **59** (6), 715-717 (1969).

Corr, J. J., M. A. Khakoo, and J. W. McConkey, "Metastable fragment production following electron impact excitation of SF_6 ," *Journal of Physics B: Atomic and Molecular Physics* **20**, 2597-2606 (1987).

Dahl, D. A. and J. E. Delmore, SIMION Version 4.0 (U. S. Department of Energy, Idaho Falls, Idaho, 1988).

Darrach, M., "Laser Induced Fluorescence Measurements on Electron-Impact Excited Molecules," Ph.D. Thesis, The University of Windsor, 1990.

DeKoven, B. M., D. H. Levy, H. H. Harris, B. R. Zegarski, and T. A. Miller, "Rotational excitation in the electron impact ionization of supercooled N_2 ," *Journal of Chemical Physics* **74** (10), 5659-5668 (1981).

Demtröder, W., *Laser Spectroscopy Basic Concepts and Instrumentation*, 1st ed. (Springer-Verlag, Berlin, 1981).

Ducrepin, M., J. Dike, R. B. Siegel, V. Tarnovsky, and K. Becker, "Optical emissions from electron-impact-excited tetra-ethoxysilane," *Journal of Applied Physics* **73** (11), 7203-7206 (1993).

Exciton Inc., "Laser Dyes," (Exciton, Inc., Dayton, Ohio, 1992).

Fano, U. and J. H. Macek, "Impact Excitation and Polarization of the Emitted Light," *Reviews of Modern Physics* **45** (4), 553-573 (1973).

Feofilov, P. P., *The Physical Basis of Polarized Emission* (Consulatants Bureau, New York, 1961).

Filippelli, A. R., C. C. Lin, L. W. Anderson, and J. W. McConkey, "Principles and Methods for Measurement of Electron Impact Excitation Cross Sections for Atoms and Molecules by Optical Techniques," in *Advances in Atomic, Molecular and Optical Physics* (1994), Vol. 33, pp. 1-62.

Finn, T. G., J. F. M. Aarts, and J. P. Doering, "High Energy-Resolution Studies of Electron Impact Optical Excitation Functions
I. The Second Positive System of N_2^* ," *Journal of Chemical Physics* **56** (11), 5632-5636 (1972).

Fons, J. T., J. S. Allen, R. S. Schappe, and C. C. Lin, "Production of electronically excited N_2^+ ions by electron impact on N_2 molecules," *Physical Review A* **49** (2), 927-932 (1994).

Frost, M., S. Kato, V. Bierbaum, and S. Leone, "Direct observation of the simultaneous transfer of vibrational energy and charge in the $^{14}N_2^+(v) + ^{14}N_2$ reaction," *Journal of Chemical Physics* **98** (7), 5993-5995 (1993).

Gilbert, P. G., R. B. Siegel, and K. Becker, "Absolute photoemission cross sections of ultraviolet emissions produced by electron-impact dissociation of boron trichloride," *Physical Review A* **41** (10), 5594-5599 (1990).

Giordmane, J. A. and T. C. Wang, "Molecular Beam Formation by Long Parallel Tubes," *Journal of Applied Physics* **31** (3), 463-471 (1960).

Goldsmith, J. E. M. and J. E. Lawler, "Optogalvanic Spectroscopy," *Contemporary Physics* **22** (2), 235-248 (1981).

Greene, C. H. and R. N. Zare, "Determination of product population and alignment using laser-induced fluorescence," *Journal of Chemical Physics* **78** (11), 6741-6753 (1983).

Hamamatsu Corp., "Photomultiplier Tubes," (Japan, 1985).

Helvajian, H., B. M. Dekoven, and A. P. Baronavski, "Laser Induced Fluorescence of $N_2(X^1\Sigma_g^+)$ and Electron Impact Excited $N_2^+(X^2\Sigma_g^+)$ in a Pulsed Supersonic Beam: Rotational Distributions," *Chemical Physics* **90**, 175-183 (1984).

Herzberg, G., *Molecular Spectra and Molecular Structure Volume I - Spectra of Diatomic Molecules*, 2 ed. (Krieger, Malabar, Florida, 1950).

Hesser, J. E. and K. Dressler, "Radiative Lifetimes of Ultraviolet Emission Systems Excited in BF_3 , CF_4 , and SiF_4 ," *Journal of Chemical Physics* **47** (9), 3443-3450 (1967).

Hippler, M. and J. Pfab, "Optogalvanic spectroscopy of argon and wavelength calibration in the near-ultraviolet," *Optics Communications* **97**, 347-352 (1993).

Inokuti, M., "Inelastic Collisions of Fast Charged Particles with Atoms and Molecules - The Bethe Theory Revisted," *Reviews of Modern Physics* **43** (3), 297-347 (1971).

Itikawa, Y., M. Hayashi, A. Ichimura, K. Onda, K. Sakimoto, K. Takayanagi, M. Nakamura, H. Nishimura, and T. Takayanagi, "Cross Sections for Collisions of Electrons and Photons with Nitrogen Molecules," *Journal of Physical and Chemical Reference Data* **15** (3), 985-1010 (1986).

Jabbour, Z. J. and K. Becker, "Analysis of optical emissions produced by dissociative electron impact on CCl_2F_2 ," *Journal of Chemical Physics* **90** (9), 4819-4825 (1989).

Jabbour, Z. J., K. A. Blanks, K. E. Martus, and K. Becker, "Continuous ultraviolet emissions produced by electron impact on SF_6 and NF_3 ," *Journal of Chemical Physics* **88** (7), 4252-4256 (1988a).

Jabbour, Z. J., K. E. Martus, and K. Becker, "Absolute photo-emission cross section of the $BCl A^1\Pi \rightarrow X^1\Sigma^+$ system produced by dissociative electron impact on BCl_3 ," *Zeitschrift für Physik D* **9**, 263-264 (1988b).

Kato, S., M. J. Frost, V. M. Biernbaum, and S. R. Leone, "A selected ion flow tube-laser induced fluorescence instrument for vibrationally state-specific ion-molecule reactions," *Review of Scientific Instruments* **64** (10), 2808-2820 (1993).

Keller, R., R. Engleman Jr., and B. A. Palmer, "Atlas for optogalvanic wavelength calibration," *Applied Optics* **19** (6), 836-837 (1980).

King, D. S., P. K. Schenck, K. C. Smyth, and J. C. Travis, "Direct calibration of laser wavelength and bandwidth using the optogalvanic effect in hollow cathode lamps," *Applied Optics* **16** (10), 2617-2619 (1977).

Kinsey, J. L., "Laser-Induced Fluorescence," *Annual Review of Physics and Chemistry* **28**, 349-372 (1977).

Krishnakumar, E. and S. K. Srivastava, "Cross sections for the production of N_2^+ , $N^+ + N_2^{2+}$ and N^{2+} by electron impact on N_2 ," *Journal of Physics B: Atomic and Molecular Physics* **23**, 1893-1903 (1990).

Lofthus, A. and P. H. Krupenie, "The Spectrum of Molecular Nitrogen," *Journal of Physical and Chemical Reference Data* **6** (1), 113-307 (1977).

Lumonics Inc., "Instruction Manual - Lumonics - Series EPD-330 Pulsed Dye Laser," (Ontario, Canada, 1982).

Lumonics Inc., "Spectrum Master Series Manual," (Lumonics Inc., Ontario, Canada, 1994), pp. 4-38 to 4-40.

Ma, C., M. R. Bruce, and R. A. Bonham, "Absolute Partial and Total Electron-Impact-Ionization Cross Sections for CF_4 from Threshold up to 500 eV," *Physical Review A* **44** (5), 2921-2934 (1991).

Malcolm, I. C., H. W. Dassen, and J. W. McConkey, "Polarisation of radiation from H_2 excited by electron impact: Lyman and Werner emissions and Lyman- α ," *Journal of Physics B: Atomic and Molecular Physics* **12** (6), 1003-1017 (1979).

Märk, T. D., "Ionization of Molecules by Electron Impact," in *Electron-Molecule Interactions and Their Applications*, edited by L. G. Christophorou (Academic Press, Inc., Orlando, Florida, 1984), Vol. 1, pp. 251-334.

Miller Jr., K. and K. Becker, "Ultraviolet and visible fluorescence produced by controlled electron impact on SO_2 ," *Canadian Journal of Physics* **65**, 530-534 (1987).

Moore, J. H., C. C. Davis, and M. A. Coplan, *Building Scientific Apparatus A Practical Guide to Design and Construction*, 1st ed. (Addison-Wesley, London, 1983).

Müller, U., T. Bubel, G. Schulz, A. Sevilla, J. Dike, and K. Becker, "Further studies of the continuous UV emission produced by electron impact on CF_4 ," *Zeitschrift für Physik D* **24**, 131-139 (1992).

Mumma, M. J., "Molecular Branching-Ratio Method for Intensity Calibration of Optical Systems in the Vacuum Ultraviolet," *Journal of the Optical Society of America* **62** (12), 1459-1466 (1972).

Nagata, T., A. Nakajima, T. Kondow, and K. Kuchitsu, "Nascent rotational distributions of $N_2^+(X^2\Sigma_g^+)$ produced by electron-impact ionization of N_2 in a supersonic beam," *Journal of Chemical Physics* **87** (11), 6507-6512 (1987).

Nestor, J. R., "Optogalvanic spectra of neon and argon in glow discharge lamps," *Applied Optics* **21** (22), 4154-4157 (1982).

Olander, D. R. and V. Kruger, "Molecular Beam Sources Fabricated from Multichannel Arrays. III. The Exit Density Problem," *Journal of Applied Physics* **41**, 2769-2776 (1970).

- Pearse and Gaydon, *The Identification of Molecular Spectra* (Wiley, 1941).
- Piper, L. G., B. D. Green, W. A. M. Blumberg, and S. J. Wolnik, "Electron impact excitation of the N_2^+ Meinel band," *Journal of Physics B: Atomic and Molecular Physics* **19**, 3327-3332 (1986).
- Radzig, A. A. and B. M. Smirnov, *Reference Data on Atoms, Molecules, and Ions* (Springer-Verlag, Heidelberg, 1985).
- Rescigno, T. N., "Low-energy electron collision processes in NF_3 ," *Physical Review A* **52** (1), 329-333 (1995).
- Rogue, M. B., R. B. Siegel, K. E. Martus, V. Tarnovsky, and K. Becker, "Production of fluorine $2,4p \rightarrow 2p^o$ resonance radiation by electron impact on SF_6 , NF_3 , and CCl_2F_2 ," *Journal of Chemical Physics* **94** (1), 341-350 (1991).
- Roth, A., *Vacuum Technology*, 3rd ed. (Elsevier Science Publishers B.V., Amsterdam, 1990).
- Shaw, M. and J. Campos, "Emission Cross Sections of the Second Positive and First Negative Systems of N_2 and N_2^+ Excited by Electron Impact," *Journal of Quantitative Spectroscopy and Radiation Transfer* **30** (1), 73-76 (1983).
- Shemansky, D. E. and J. M. Ajello, "The Saturn Spectrum in the EUV - Electron Excited Hydrogen," *Journal of Geophysical Research* **88** (1), 459-464 (1983).
- Stanton, P. N. and R. M. St. John, "Electron Excitation of the First Positive Bands of N_2 and of the First Negative and Meinel Bands of N_2^+ ," *Journal of the Optical Society of America* **59** (3), 252-260 (1969).
- Stellar Software, Beam Two Optical Ray Tracer (Stellar Software, Berkeley, Ca., 1989).
- Tokue, I., T. Honda, and Y. Ito, *Chemical Physics* **140**, 157 (1990).
- Van Brunt, R. J. and R. Zare, N., "Polarization of Atomic Fluorescence Excited by Molecular Dissociation," *Journal of Chemical Physics* **48** (9), 4304-4308 (1968).
- Van der Burgt, P. J. M. and J. W. McConkey, "Metastable fragment production by electron-impact dissociation of CF_4 ," *Journal of Physics B: Atomic and Molecular Physics* **24**, 4821-4830 (1991).
- Van der Burgt, P. J. M., W. B. Westerveld, and J. S. Risley, "Photoemission Cross Sections for Atomic Transitions in the Extreme Ultraviolet due to Electron Collisions with Atoms and Molecules," *Journal of Physical and Chemical Reference Data* **18** (4), 1757-1805 (1989).
- Van Zyl, B., M. W. Gealy, and H. Neumann, *Physical Review A* **31**, 2922-2931 (1985).
- Wang, S., J. L. Forand, and J. W. McConkey, "Dissociative excitation of CF_4 by controlled electron impact," *Canadian Journal of Physics* **67**, 699 (1989).

Weast, R. C., "CRC Handbook of Chemistry and Physics," (CRC Press, Inc., Boca Raton, Florida, 1980).

Winters, H. F. and M. Inokuti, "Total Dissociation Cross Section of CF_4 and other fluoroalkanes," *Physical Review A* **25** (3), 1420-1430 (1982).

Woolsey, J. M., J. L. Forand, and J. W. McConkey, "Lyman- α revisted," *Journal of Physics B: Atomic and Molecular Physics* **19**, L493-L497 (1986).

Young, B. (Personal Communication).

Zetner, P. W., M. Darrach, P. Hammond, W. B. Westerveld, R. L. McConkey, and J. W. McConkey, "Rotationally Resolved Electron-Impact Ionization of N_2 in a Supersonic Jet," *Chemical Physics* **124**, 453-464 (1988).

Zipf, E. C., "Dissociation of Molecules by Electron Impact," in *Electron-Molecule Interactions and their Applications*, edited by L. G. Christophorou (Academic Press, Inc., Orlando, Florida, 1984), Vol. 1, pp. 335-401.

Zugenmaier, P., "Zur Theorie der Molekularstrahlerzeugung mit Hilfe zylindrischer Rohre," *Zeitschrift für angewandte Physik* **20**, 184-188 (1965).