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VUV SPECTROSCOPIC INVESTIGATIONS OF ELECTRON COLLISIONS
WITH GROUND STATE AND METASTABLE TARGETS

By

SHOUYE WANG

A Dissertation
Submitted to the
Faculty of Graduate Studies and Research
through the Department of Physics in Partial Fulfillment
of the Requirements for the Degree of Doctor of Philosophy
at the University of Windsor

Windsor, Ontario, Canada

1991
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ABSTRACT

VUV SPECTROSCOPIC INVESTIGATIONS OF ELECTRON COLLISIONS
WITH GROUND STATE AND METASTABLE TARGETS

by

Shouye Wang

A detailed description of a calibration technique is given in which emissions from H and H_2 are used to calibrate the optical apparatus used for electron impact emission cross section measurements in the wavelength range 90-130 nm. Absolute emission cross sections for the KrII 96.5 nm and KrII 91.7 nm have been established to be 3.4 \times 10^{-18} \text{cm}^2 and 2.8 \times 10^{-18} \text{cm}^2 respectively at 200 eV. The cross section ratio of these two lines has been determined to be constant over the energy range 100-300 eV. Dissociative excitation and fragmentation of CF_3H following electron impact have been studied over the energy range up to 600 eV by monitoring the VUV radiation in the wavelength region 50-130 nm produced from excited fragments. Emission cross sections for production of individual features have been established. R.F.discharge-produced metastable N_2 target has been used in collisions with electrons. Intensity change patterns of the LBE band system and the Carroll-Yoshino band system indicate that more than 20% of the N_2 molecules in the discharge have been promoted from the normal \nu=0 ground vibrational level.
The absolute emission cross sections for atomic oxygen resonance lines at 130.3 nm, 98.9 nm, 87.8 nm and 102.7 nm following electron impact on atomic oxygen have been established up to 100 eV. About 70% of NO molecules are dissociated by an r.f.-discharge source to provide a high concentration of atomic oxygen in the target beam. Extreme care has been taken to measure the trapping reduction in the emission rate for these resonance lines. Present results are able to remove some discrepancies in previous measurements, and provide cross section data with a much higher level of reliability.
To my wife, Li Lang, and my son, Boyu, who have sacrificed so much in their family life to make my research enjoyable and meaningful by showing their love and support for me, and for this work as well.
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CHAPTER I: INTRODUCTION

Collisions between electrons and atoms (or molecules) have long been used as a powerful tool to study the detailed physical processes involved in the interaction between the projectile and the target. Collisional physics can be studied either by monitoring the emitted photons induced by electron impact on the target, or by detecting the scattered electrons and charged particles produced during the collision. The cross section determination is one of the most important measurements in collision experiments, and it can be performed by observing the outgoing photons or the scattered electrons. In many cases, particularly in the dissociative excitation of multi-atom molecules, it is impossible to identify individual states in the scattered electron channel. However, observation of the emitted photons allows unambiguous identification and study of a particular state with high resolution.

The relatively easy and direct identification of the VUV spectrum in the wavelength region 50–200 nm gives the excitation details of the transitions involved. Often each spectral line can be isolated for study by properly choosing the wavelength setting and slit widths of the monochromator. The energy dependence of each excitation process can be determined by observing the photon intensity variation with electron energy. This is especially important near threshold, where many channels can contribute to the excitation process. Since VUV emissions are often the result of transitions to the ground states of the target, cascade from higher states can often significantly affect the excitation cross section evaluations, and trapping of resonance radiations can
reduce the emission rate significantly at high gas pressure. Fortunately, the cascade contribution can often be measured or estimated. It has always been a challenge to make absolute intensity measurements in the VUV region because of a lack of standards for the calibration of the photon detection system and the consequent difficulty of normalization of the cross section data. Over the past few years, great progress has been made in VUV emission cross section measurements. The cross section for excitation of Lyman-α at 121.6 nm has been established by many independent groups <42,46>. Relative and absolute calibration of VUV photon detection systems has been greatly improved by using synchrotron radiation <23> or molecular branching ratio techniques <46,49,52,53,69>.

A number of factors motivated the present work. There is a continuing demand for cross section data from the plasma physics, particularly the plasma processing community. In a discharge, fluorine atoms are chemically active and play an important role in the chemical etching of the semiconductor materials <55>. Optimization of plasma parameters and proper modeling of the processes within a plasma reactor require absolute cross section data for fragmentation of F-containing molecules by electron impact. Previous work from this laboratory had investigated the break up of SF₆ <57> and CF₄ <58>. This thesis reports the extension of this work to CF₃H <148>.

A continuing motivation for careful excitation cross section measurements in the VUV region has been the need to establish secondary standards in this wavelength region. Of particular interest in this connection are
transitions in the rare gases which can act as convenient reference
gases. Excitation of the \( nsnp^6 \, ^2S_{1/2} \) states of the heavy rare gas ions
produce transitions to the ground state which are free from resonance
trapping and polarization effects. Thus, they provide ideal candidates
for secondary standards. The KrII lines at 96.5 and 91.7 nm could not
be used because previous measurements, even on the ratio of the cross
sections of the two lines, differed by more than a factor of two <149>.
The present work was carried out to remove the discrepancy. Spectral
resolution and resonance trapping effects have been shown to play
important roles in the measurement and probably explain the divergence
in the previous results.

A final motivation for the present work was to get involved in
experiments involving electron collisions with excited or metastable
targets. These experiments are at the cutting edge of research in the
field of electron impact excitation of atoms and molecules and have
profound significance in a number of fields such as plasma physics and
the physics of planetary atmospheres. As a first step in this direction,
we have sought to use our existing R.F.discharge source, which has
proved very suitable for producing high dissociation fractions in \( H_2 \)
<69>, and explore its performance with various gas mixtures involving
\( N_2 \), He, \( SF_6 \) and NO. We have been able to find conditions in which more
than 20% of the \( N_2 \) molecules in the source have been promoted from the
normal \( v=0 \) ground vibrational level. Sufficient target populations of N
atoms have been obtained to enable relative cross sections for the NI
120 nm emission to be obtained in the energy region below the onset for
dissociative excitation of this line from the parent molecule.
The excitation of atomic oxygen by photoelectrons in the thermosphere and by precipitating electrons in auroral substorms has been the subject of many investigations for the last twenty years <110>. Interest in these aeronomic problems and the need for accurate electron scattering cross sections of atomic oxygen arise partly because inelastic electron scattering off atomic oxygen is a major factor in the determination of electron cooling rates and thermal energy balance in these regions. Satellite and rocket observations of the airglow and aurora show that the VUV radiations emitted by atomic oxygen and its ions dominate the spectrum from 50 nm to 140 nm <108,109>. The numerous OI and OII resonance transitions and their cascade contributions provide a unique opportunity to study quantitatively the optical trapping problems <129>. The observation of the OI and OII emissions in the VUV region from the ground and from satellites provides a remote-sensing technique for studies of the chemistry and dynamics of atomic oxygen in the atmosphere <140,143>. Unfortunately, the investigation of these interesting problems has been hindered by a lack of accurate cross section data. The VUV emission cross sections of atomic oxygen by electron impact were first measured by Stone and Zipf in the early 1970's <118>, but their data conflicted with theoretical calculations and analyses of spectra from satellite and rocket observations of the atomic oxygen emissions. Recently, this group <83> revised their cross sections, and reduced previous data by a factor of 2.8, removing some of the long standing discrepancies. However, recent electron energy loss studies of atomic oxygen by Doering et al. <113-115>, suggested that Zipf's cross section for OI 98.9 nm emission is still about a factor of 2 larger than it should be. The energy dependence of Zipf's data <83> for OI 98.9 nm
emission feature also differs widely from Doering's work <115>. As suggested by both groups, further investigations are necessary to provide reliable cross section data for use in the modeling of the processes involving electron scattering from atomic oxygen.

This situation has motivated the present work on atomic oxygen. We have been able to use our R.F. discharge source with NO to produce large quantities of atomic oxygen in our target beam. A comprehensive study of VUV emissions of atomic oxygen at 130.3 nm, 98.9 nm, 102.7 nm, and 87.8 nm has been made for impact energies up to 100 eV. Present results are able to explain some discrepancies in other previous measurements. However, detailed comparisons with earlier work have revealed serious discrepancies in some instances. These are discussed in detail in the text.
CHAPTER II: THEORY

2.1 QUANTUM THEORY OF SCATTERING

Consider a collisional excitation process of a two-body system which
consists of an incident electron and a ground state atom (or molecule)
with z electrons. When the incident electron is sufficiently fast (i.e.,
with high kinetic energy) but still nonrelativistic, the differential cross
section $d\sigma_n$ calculated in the first Born approximation (in the lowest
order in the interaction $V$ between the incident electron and the target
atom) for scattering into the solid angle $d\omega$ located at $\theta$ and $\phi$ in atomic
units is given by \(1-3\):

$$
d\sigma_n = \frac{m^2 e^2}{4\pi^2 p_0} \left[\int \, e^{i\vec{K} \cdot \vec{r}} \, u_n^*(\vec{r}_1 \ldots \vec{r}_z) V u_0(\vec{r}_1 \ldots \vec{r}_z) d\vec{r}_1 \ldots d\vec{r}_z d\vec{r} \right]^2 d\omega \tag{2-1}
$$

where

$$
\vec{K} = \vec{p}' - \vec{p}_0 \tag{2-2}
$$

$\vec{p}'$ is the momentum of the electron after collision, $\vec{p}_0$ is the momentum
of the electron before collision, $m$ is the reduced mass of the two body
system, $V$ is the interaction between the incident electron and the target
atom, $u_n$ and $u_0$ are the bound state wave functions of the target atom
at the $n$th level and ground level respectively, $\vec{r}$ is the position of the
incident electron relative to the target atom, and $\vec{r}_i$ is the position of
the $i$th atomic electron. When the interaction is coulombic, i.e., when $V$ is
written as

-6-
\[ V = \sum_{j=1}^{x} \frac{e^2}{|\vec{r} - \vec{r}_j|} - z \frac{e^2}{r} \quad (2-3) \]

Bethe recognized that it is advantageous to perform first the integration over \( \vec{r} \) by using the relation \( \langle 4 \rangle \)

\[
\int \frac{e^{i \vec{r} \cdot \vec{r}_j}}{|\vec{r} - \vec{r}_j|} d\vec{r} = \frac{4\pi}{K^2} e^{i \vec{r} \cdot \vec{r}_j} \quad (2-4)
\]

Thus Equation (2-1) transforms into

\[
\frac{d\sigma_n}{K^4 p_0} = \frac{4m^2 e^4 P}{\epsilon_n(K)^2} d\omega \quad (2-5)
\]

where \( \epsilon_n(K) \) is an atomic matrix element given by

\[
\epsilon_n(K) = \langle n / \sum_{j=1}^{x} e^{i \vec{r} \cdot \vec{r}_j} / 0 \rangle \\
= \int u_n^* \sum_{j=1}^{x} e^{i \vec{r} \cdot \vec{r}_j} u_0 d\vec{r}_1 \ldots d\vec{r}_x \quad (2-6)
\]

The second term in Equation (2-3) gives no contribution owing to the orthogonality of states \( n \) and \( 0 \). Replace \( d\omega \) by \( 2\pi \sin \theta d\theta = \frac{d\Omega(K^2)}{p \rho_s} \) in Equation (2-5) to obtain
\[ d\sigma_n = \frac{4\pi m^2 e^4}{p^2 K^4} /\varepsilon_n(K)/^2 d(K^2) \] (2-7a)

\[ = \frac{4\pi m^2 e^4}{p^2 K^2} /\varepsilon_n(K)/^2 d\ln(K\alpha_0)^2 \] (2-7b)

where \( \alpha_0 = \frac{\hbar^2}{4\pi^2 m_e e^2} \) is the Bohr radius.

We now define

\[ f_n(K) = \frac{E_{n0}}{R(K\alpha_0)^2} /\varepsilon_n(K)/^2 \] (2-8)

Where \( f_n(K) \) is so-called Generalized Oscillator Strength, \( R = m_e e^4/2 \) is the Rydberg energy, and \( E_{n0} \) is the excitation energy from the ground state to the \( n \)th excited state. If we substitute Equation (2-8) in Equation (2-7 b), this gives

\[ d\sigma_n = \frac{4\pi e^4 m^2 \alpha_0^2 R}{p^2 E_{n0}} f_n(K) d\ln(K\alpha_0)^2 \] (2-9)

For the collision of an electron and an atom (assumed stationary because of its much larger mass) the relative momentum \( p_0 \) is given by

\[ p_0 = m v \] (2-10)

Equation (2-9) becomes

\[ d\sigma_n = \frac{4\pi R^2 \alpha_0^2}{TE_{n0}} f_n(K) d\ln(K\alpha_0)^2 \] (2-11)
Where $T = m_e v^2 / 2$ is the kinetic energy of the incident electron. $m_e$ is the mass of electron. The total cross section is equal to the integration of Equation (2-11) over all possible values of $\ln(K\alpha_0)^2$, that is

$$
\sigma_n = \frac{4\pi \alpha_0^2 R^2}{TE_{no}} \int_{\ln(K\alpha_0)_{\text{min}}}^{\ln(K\alpha_0)_{\text{max}}} f_n(K) \, d\ln(K\alpha_0)^2 
$$

(2-12)

This is the expression of the effective excitation cross section of the transition from the ground state to the $n$th excited state following electron impact on an initially stationary atom.

Bethe [5-6] developed a technique of expressing $\sigma_n$ in terms of an asymptotic expansion in inverse powers of $T$. This approximation is excellent at high energy limit. From the result of Born approximation for $\sigma_n$ expressed by Equation (2-12), it is clear that the central part of the asymptotic expansion must be concerning the behaviors of the upper and the lower integral limits $\ln(K\alpha_0)_{\text{max}}$ and $\ln(K\alpha_0)_{\text{min}}$ as well as the Generalized Oscillator Strength $f_n(K)$. It is known that the optical oscillator strength $f_n$ is equal to the asymptotic form of the Generalized Oscillator Strength as $K \to 0$

$$
f_n = \lim_{K \to 0} f_n(K) 
$$

(2-13)

In the optically forbidden process, the optical oscillator strength vanishes
Thus the Generalized Oscillator Strength $f_n(K)$ goes to zero as $K$ approaches its lower limit defined by $(K\alpha_0)^2 \rightarrow \frac{1}{7}$. Bethe theory is based on high energy approximation by which $\ln((K\alpha_0)^2)_{\text{max}}$ and $\ln((K\alpha_0)^2)_{\text{min}}$ take their values as $\ln((K\alpha_0)^2)_{\text{max}} \rightarrow -\infty$ and $\ln((K\alpha_0)^2)_{\text{min}} \rightarrow -\infty$ respectively without causing much error $<7-8>$. Finally, Bethe theory $<9>$ gives the expressions for the excitation cross sections of optically allowed and optically forbidden processes respectively as

\[
\sigma_n = \frac{4\pi \alpha_0^2 R}{T} \left( M_n^2 \ln\left( \frac{4C_n T}{R} \right) + \frac{\gamma_n R}{T} + O\left[ \left( \frac{E_{\text{no}}}{T} \right)^2 \right] \right)
\]

for optically allowed \hspace{1cm} (2-15)

\[
\sigma_n = \frac{4\pi \alpha_0^2 R}{T} \left( b_n + \frac{\gamma_n R}{T} + O\left[ \left( \frac{E_{\text{no}}}{T} \right)^2 \right] \right)
\]

for optically forbidden \hspace{1cm} (2-16)

where $M_n^2 = f_n R / E_{\text{no}}$ is the dipole matrix element, and

\[
\gamma_n = -\frac{m f_n}{2m} - \left. \frac{d f_n(K)}{4R} \right|_{K=0}
\]

\[
b_n = \int_{-\infty}^{R} \frac{f_n(K)}{E_{\text{no}}} \ d\ln(K\alpha_0)^2
\]

At the extremely high energy limit $T \rightarrow \infty$, Equations (2-15) and (2-16)
reduce to

\[ \sigma_n = \frac{4\pi a_0^2 R M_n^2 \ln T}{T} + \frac{C}{T} \] for optically allowed \hspace{1cm} (2-19) \]

\[ \sigma_n = \frac{4\pi a_0^2 R b_n}{T} \] for optically forbidden \hspace{1cm} (2-20) \]

where \[ C = 4\pi a_0^2 R M_n^2 \ln \left( \frac{4C_n}{R} \right) \] \hspace{1cm} (2-21) \]

From (2-19), one knows that for an optically allowed process with sufficiently large incident energy \( T \), a plot of \( \sigma_n T \) versus \( \ln T \) would produce a straight line with its slope proportional to \( M_n^2 \) and hence to \( f_n \). Therefore if the accurate values of the optical oscillator strength are available, it is possible to normalize the relative measurements of the cross section to an absolute scale. The intercept with the horizontal axis yields a value of \( C_n \). This is so-called the Fano plot indicated by Fano in 1954 <10>. If the Fano plot shows a straight line behavior over an interval of large energy \( T \) values, it indicates the applicability of the Bethe theory in that energy interval. If the absolute cross section data are available, the values of the slope and the intercept may be extracted and hence the optical oscillator strength can be obtained. For the optically forbidden process with high energy limit, the plot of \( \sigma_n T \) will be a constant value which gives the information about \( b_n \).

2.2 PHOTON SPECTROSCOPY

2.2.1 EXCITATION CROSS SECTION
Consider a multichannel scattering process such as electron and molecule collision in a cross-beam experiment. When the pressure of gas atoms and electron current are sufficiently low, the secondary processes, such as atom-atom collisional population and depopulation and resonance absorption, can be neglected, the number density of \( n(j) \) of the jth excited state atoms in the collision region is given by the following equation

\[
\frac{dn(j)}{dt} = - \sum \left( n(j)A(jk) \right) + \frac{n(g)Q(j)L}{e} + \sum A(ij)n(i) \quad (2-22)
\]

Where \( Q(j) \) is the excitation cross section of the transition from the ground state to the jth excited state. \( n(g) \), \( n(i) \), and \( n(j) \) are the number densities of the ground, ith and jth excited state atoms respectively. \( I \) is the electron current. \( e \) is the electron charge. \( A(ij) \) is the Einstein A coefficient for the transition from the ith state to the jth state. \( L \) is the interaction length of the electron-atom intersection.

The first term in (2-22) gives the rate at which the jth excited state atoms decay to the lower states k through radiation; and the second term describes the electron impact excitation of atoms from the ground state to the jth excited state. The third term defines the cascade contribution. When the system reaches the equilibrium state, one has

\[
\frac{dn(j)}{dt} = 0 \quad \text{at equilibrium} \quad (2-23)
\]
Thus (2-22) becomes

\[ n(j) = \left[ \frac{n(g)Q(j)IL}{e} + \sum_{i:j} A(ij)n(i) \right] L \sum_{k:j} A(jk) \]  

\[ (2-24) \]

Define \( J(jk) \) to be the rate at which atoms in state \( j \) decay to state \( k \) per unit length of electron beam as

\[ J(jk) = \frac{n(j)A(jk)}{L} \]  

\[ (2-25) \]

Substitute (2-24) in (2-25), this follows

\[ J(jk) = \left[ \frac{n(g)Q(j)I}{e} + \sum_{i:j} J(ij) \right] A(jk)/L \sum_{k':j} A(jk') \]  

\[ (2-26) \]

In terms of the excitation cross section \( Q(j) \), the above equation can be written as

\[ Q(j) = \left[ \frac{J(jk)}{B(jk)} - \sum_{i:j} J(ij) \right] e/n(g)I \]  

\[ (2-27) \]

where

\[ B(jk) = \sum_{k':j} A(jk') \]  

\[ (2-28) \]

is the branching ratio for the \( j-k \) transition. If cascade contribution is negligible under certain circumstances, Equation (2-27) simply reduces to
\[ Q(j) = \frac{J(jk)}{B(jk)n(g)I} \]  
\[ = \sum_{k',e} J(jk')e/n(g)I \]  

From Equations (2-27) and (2-29), one can determine the excitation cross section by measuring the radiation emitted in the transitions originating from and terminating in state \( j \). In the photon spectroscopy experiment, the intensity of a certain spectral line, \( J(jk) \), is often measured, which gives the determination of effective cross section \( Q(jk) \) as

\[ Q(jk) = \frac{J(jk)e}{n(g)I} \]  

If we replace \( J(jk) \) by (2-26), then (2-30) becomes

\[ Q(jk) = \left[ Q(j) + \sum_{i'} Q(i') \right] B(ij) \]  

2.2.2 POLARIZATION CONSIDERATIONS

We take the electron beam direction as \( z \) axis, and the gas beam as \( y \) axis. Let \( I_{11} \) be the intensity of radiation (per unit solid angle obtained in the \( x \) direction) with electric field parallel to the \( z \) direction and \( I_{1} \) be the intensity of radiation with electric field perpendicular to the \( z \) direction. The polarization of radiation is defined by
\[ P = \frac{I_{11} - I_1}{I_{11} + I_1} \quad (2-31) \]

The flux of photons emitted into unit solid angle in the direction described by a polar angle \( \theta \) for \( j-k \) transition was obtained by Heddle and Keesing <11> in 1968 as

\[
J(jk, \theta) = I_{11}(jk)\sin^2\theta + I_1(jk)\cos^2\theta + I_1(jk) \\
= [I_{11}(jk) + I_1(jk)](1 - P\cos^2\theta) \quad (2-32a)
\]

\[
= [I_{11}(jk) + 2I_1(jk)](1 - P\cos^2\theta) \quad (2-32b)
\]

Integrating (2-32a) over all angles \( \theta \) and \( \phi \) gives the total intensity for the \( j-k \) transition.

\[
J(jk) = \int_{4\pi} J(jk, \theta) \, d\omega \\
= \frac{8\pi}{3}[I_{11}(jk) + 2I_1(jk)] \\
= \frac{8\pi}{3}\frac{[I_{11}(jk) + 2I_1(jk)]a}{n(g)l} \\
\quad (2-33)
\]

Thus

\[
Q(jk) = \frac{J(jk)a}{n(g)l} \\
= \frac{8\pi\sqrt{[I_{11}(jk) + 2I_1(jk)]}a}{3n(g)l} \\
\quad (2-34)
\]

By measuring \( I_{11} \) and \( I_1 \), one can determine the effective cross section \( Q(jk) \) using the relation (2-34). The differential cross section is defined by
\[ q(jk, \theta) = \frac{J(jk, \theta) a}{n(g) I} \quad (2-35a) \]

From (2-32b)

\[ = a(jk)(1 - P \cos^2 \theta) \quad (2-35b) \]

Where

\[ a(jk) = \frac{e(I_{11} + I_1)}{n(g) I} \quad (2-36a) \]

\[ = q(jk, 90^\circ) \quad (2-36b) \]

The effective cross section is the integration of \( q(jk, \theta) \) over a 4\( \pi \) solid angle.

\[ Q(jk) = \int_{4\pi} q(jk, \theta) \, d\omega \]

\[ = 4\pi q(jk, 90^\circ) \left( 1 - \frac{P}{3} \right) \quad (2-37) \]

Thus, the effective cross section is proportional to the differential cross section at an observation angle \( \theta = 90^\circ \) which is the arrangement of apparatus used in this work.

The efficiency of a photon detecting system is often polarization sensitive, that is, if one assumes that \( k_{11} \) and \( k_1 \) are the detecting efficiencies of the system for the radiations polarized with their electric field parallel and perpendicular to the entrance slit of the monochromator respectively, one finds that \( k_{11} \) and \( k_1 \) are often quite different.

This instrumental polarization sensitivity produces a few corrections to the previous formula. Following the treatment of Clout and Heddle <12>, let's consider a cross beam arrangement. The radiation is observed at an angle \( \theta \) to the electron beam direction, and an angle \( \alpha \) between the plane
of the electron beam - the optical axis and the entrance slit (see Figure 2.3 in the reference <13>). Then, the observed signal is given by (omit the state indices \( j, k \))

\[
S(\theta, \alpha) = l_{11} (k_{11} \cos^2 \alpha \sin^2 \theta + k_{1} \sin^2 \alpha \sin^2 \theta) \\
+ l_{1} [k_{11}(\sin^2 \alpha \cos^2 \alpha \cos^2 \theta) + k_{1}(\cos^2 \alpha + \sin^2 \alpha \cos^2 \theta)]
\] (2-38)

Thus, by suitably choosing the \( \alpha \) and \( \theta \), one can reduce the expression (2-38). We set \( \theta = 90^\circ \), \( \alpha = 90^\circ \), then (2-38) becomes

\[
S(90^\circ, 90^\circ) = l_{11}k_{11} + l_{1}k_{11} = k(l_{11} + l_{1}) \quad \text{if} \quad k_{1} - k_{11} < k
\] (2-39a)

from (2-32a)

\[
kJ(jk, 90^\circ)
\] (2-39c)

from (2-36b)

\[
\frac{n(g)kIq(jk, 90^\circ)}{e}
\] (2-39d)

from (2-37)

\[
\frac{n(g)kIq(jk)}{4\pi e(1 - \frac{q}{j})}
\] (2-39e)

However, if the radiation has zero polarization, (i.e., \( l_{11} = l_{1} \)), then (2-39a-e) become

\[
S(90^\circ, 90^\circ) = (k_{11} + k_{1})I
\] (2-40a)

\[
\frac{(k_{11} + k_{1})J(jk, 90^\circ)}{2}
\] (2-40b)

\[
\frac{(k_{11} + k_{1})n(g)Iq(jk, 90^\circ)}{2e}
\] (2-40c)

\[
\frac{(k_{11} + k_{1})n(g)Iq(jk)}{8\pi e}
\] (2-40d)
It is obvious that signal $S(90^\circ, 90^\circ)$ is proportional to the effective cross section $Q(jk)$ for the case of either zero polarization or equal instrumental polarization sensitivity.

If we choose $\alpha = 45^\circ$ and $\theta = \theta_0 = 54^\circ 44'$, where $\theta_0$ satisfies the relation:

$$\cos^2 \theta_0 = \frac{1}{3} \quad (2-41)$$

and

$$\theta_0 = 54^\circ 44' \quad (2-42)$$

Then Equation (2-38) reduces to

$$S(54^\circ 44', 45^\circ) = \frac{(k_{11} + k_1)(I_{11} + 2I_1)}{3} \quad (2-43a)$$

from (2-34) \[ - \frac{n(g)I(k_{11} + k_1)Q(jk)}{8ne} \quad (2-43b) \]

The angle $\theta = 54^\circ 44'$ is so called "magic angle". If one makes the measurement at the "magic angle", no polarization correction is needed, and the signal $S(54^\circ 44', 45^\circ)$ is directly proportional to the effective cross section $Q(jk)$ by Equation (2-43b). Polarization corrections need to be applied especially in atomic excitation, for example, atomic oxygen in Chapter VIII.

2.3 GAS FLOW THROUGH TUBES AND ORIFICES

The number density of the target gas in the collision region is a very important parameter in the absolute cross section measurement, and it is
impossible to accurately determine this parameter directly in the cross beam apparatus used in this work. However, by measuring the pressure close to the gas inlet, we can relate this pressure to the number density of the target gas beam by using the theory of gas flow through tubes and orifices discussed in this section.

The flow rate $F$ is defined $<14,15>$ as the product of the volumetric flow rate $\frac{dV}{dt}$ across a plane and the pressure $P$ at which it is measured, that is,

$$ F = P \frac{dV}{dt} \quad (2-44) $$

Note that this is a conventional definition used in vacuum technology, in which a constant factor $(1/kT)$ has been omitted. From the ideal gas law, it follows that

$$ F = nkT \frac{dV}{dt} $$
$$ = nkT \ S $$
$$ = nkT \ vA \quad (2-45) $$

where $k$ is the Boltzmann constant, $T$ is the absolute temperature, $S=dV/dt$ is the pumping speed, $v$ is the flow velocity, and $A$ is the cross sectional area of the tube. Another quantity called the Conductance is defined as $<16>$
where $P_2$ is the upstream pressure (measured at the entrance to a channel), and $P_1$ is the downstream pressure (measured at the exit). This quantity corresponds to the rate of flow per unit difference of pressure between two ends of the channel which was a single capillary in this work. Roth $<16>$ gave an expression for the Conductance of a general case in 1982 as

$$C = C_m J$$  \hspace{1cm} (2-47)

where $C_m$ is the Conductance for molecular flow, and $J$ is given by

$$J = \frac{C_v}{C_m} + \frac{1 + \frac{\sqrt{\frac{\pi^4 D^2 P}{\eta}}}{1.24 \sqrt{\frac{m}{\pi^2 D^2 P}}} \frac{D P}{\eta}}{1 + \frac{\sqrt{\frac{\pi^4 D^2 P}{\eta}}}{1.24 \sqrt{\frac{m}{\pi^2 D^2 P}}} \frac{D P}{\eta}}$$  \hspace{1cm} (2-48)

where

$$C_v = \frac{\pi D^4 \overline{P}}{128 L \eta}$$  \hspace{1cm} (2-49)

$$C_m = \frac{D^3 \sqrt{\frac{2 \pi k T}{m \eta}}}{6 L}$$  \hspace{1cm} (2-50)

$\overline{P}$ is the average pressure between the ends of the tube, $R_0$ is the universal gas constant, $D$ is the diameter of the tube, $L$ is the length of the tube, $\eta$ is the coefficient of viscosity, and $C_v$ is the Conductance for viscous flow. Define the pressure $C_m$ as the molecular-viscous intersection pressure in the case that $C_v = C_m$. 

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\[
\frac{C_v}{C_m} = 1 = \frac{6\pi}{128\eta} \sqrt{\frac{m}{2\pi R_0 T}} \Delta P_m \tag{2-51}
\]

or
\[
\bar{P}_m = \frac{128\eta}{6\pi D} \sqrt{\frac{2\pi R_0 T}{m}} \tag{2-52}
\]

Define a variable \( \delta \) as
\[
\delta = \frac{\bar{P}}{\bar{P}_m} \tag{2-53}
\]

Then Equation (2-48) becomes
\[
J = \delta + \frac{1 + 17\delta}{1 + 21\delta} \tag{2-54}
\]

These equations are valid for any gases. However, they are valid only for the cases that flow rate is the same over entire length of the tube, i.e., no molecules are trapped anywhere along the tube. For the general case, we consider an interval \( dL \) of the tube. The pressure drop over this interval is \( dP \). The pressure over it is \( P \) which can be considered as a constant inside this small volume provided that \( dL \) is infinitesimally small. Thus, Equation (2-46) becomes
\[ F = C\, dP \]

from (2-50)
\[ = D^3 \sqrt{\frac{2 \pi \delta_0^2}{m}} \frac{J}{6dL} \, dP \]  \hspace{1cm} (2-55)

\[ i.e., \]
\[ F dL = D^3 \sqrt{\frac{2 \pi R_0 T}{m}} J dP \]

from (2-53, 54)
\[ = D^3 \sqrt{\frac{2 \pi R_0 T}{m}} \left[ \frac{P}{P_m} + \frac{1 + 17 \frac{P}{P_m}}{1 + 21 \frac{P}{P_m}} \right] dP \] \hspace{1cm} (2-56)

Integrating (2-56) over \( L \) and \( P \), since flow \( \therefore F \) is the same over the entire tube, we finally get

\[ F = \frac{D^3}{6L_0} \sqrt{\frac{2 \pi R_0 T}{m}} P_m \left[ \frac{1}{2} \left( \frac{P_1}{P_m} \right)^2 + \frac{17P_1}{21P_m} + \frac{4}{441} \ln \left( 1 + \frac{21P_1}{P_m} \right) \right] \]

\[ - \left[ \frac{1}{2} \left( \frac{P_2}{P_m} \right)^2 + \frac{17P_2}{21P_m} + \frac{4}{441} \ln \left( 1 + \frac{21P_2}{P_m} \right) \right] > \] \hspace{1cm} (2-57)

The downstream pressure \( P_1 \) is measured at the capillary exit to the main chamber where the pressure is usually \( 10^{-6} \) torr. Therefore, \( P_1 \) is much smaller than \( P_2 \) which usually has value of 10-50 millitorr, and furthermore, the molecular-viscous intersection pressure \( P_m \) is much larger than the gas pressure used in the experiment. Thus we can omit the term including \( P_1 \) in Equation (2-57) to get

\[ F = \frac{D^3}{6L_0} \sqrt{\frac{2 \pi R_0 T}{m}} P_m \left[ \frac{1}{2} \left( \frac{P_2}{P_m} \right)^2 + \frac{17P_2}{21P_m} + \frac{4}{441} \ln \left( 1 + \frac{21P_2}{P_m} \right) \right] \]

\[ \text{from (2-50)} = C_m P_m \left[ \frac{1}{2} \left( \frac{P_2}{P_m} \right)^2 + \frac{17P_2}{21P_m} + \frac{4}{441} \ln \left( 1 + \frac{21P_2}{P_m} \right) \right] \] \hspace{1cm} (2-58)
Combining (2-58) with (2-45) gives an expression for the number density of the target gas as

\[
n = \frac{C_m \bar{P}_m}{kT S} \left[ \frac{1}{2} \left( \frac{P_2}{\bar{P}_m} \right)^2 + \frac{17P_2}{21 \bar{P}_m} - \frac{4}{441} \ln \left( 1 + \frac{21P_2}{\bar{P}_m} \right) \right] \quad (2-59)
\]

\[= \frac{C_m}{kTS} f(P_2, \bar{P}_m) \quad (2-60)\]

where \( f(P_2, \bar{P}_m) = \bar{P}_m \left[ \frac{1}{2} \left( \frac{P_2}{\bar{P}_m} \right)^2 + \frac{17P_2}{21 \bar{P}_m} + \frac{4}{441} \ln \left( 1 + \frac{21P_2}{\bar{P}_m} \right) \right] \quad (2-61)\]

Since from Equation (2-50) \( C_m \propto \sqrt{T/m} \) and \( S \propto \sqrt{T/m} A \) (\( \nu \) is the flow velocity of the gas), so that \( C_m / S \) is a factor totally dependent upon the geometry of the experimental setup. We write this factor as \( G_0 \):

\[G_0 = \frac{C_m}{S} \quad (2-62)\]

Thus, Equation (2-60) becomes

\[n = \frac{G_0}{kT} f(P_2, \bar{P}_m) \quad (2-63)\]

When gas pressure is sufficiently low so that the molecular flow condition holds, i.e., \( P_2 / \bar{P}_m \ll 1 \), thus

\[\frac{4}{441} \ln \left( 1 + \frac{21P_2}{\bar{P}_m} \right) \approx \frac{4P_2}{21 \bar{P}_m} \quad (2-64)\]

Omitting the squared term, the Equations (2-61) and (2-63) are simplified

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to the form

\[ f(P_2, \bar{P}_n) = P_2 \quad (2-65) \]

\[ n = \frac{G_0}{kT} P_2 \quad (2-66) \]

Thus, the number density of the target gas is directly proportional to the gas pressure at the entrance to the capillary under the molecular flow condition.

Lew \cite{17} derived an expression for the number density of the gas beam under the molecular flow condition in 1967 as

\[ n = \frac{G P_0}{kT} \quad (2-67) \]

G is a factor which is only dependent upon the geometry of the system. \( P_0 \) is the pressure at the entrance of the nozzle. Note that the Equations (2-66) and (2-67) are exactly the same.

If we re-write the instrumental polarization in Equation (2-39 e), \( k, \) as \( \xi, \) and substitute Equation (2-63) in (2-39 e), we get the signal for the j-k line emission observed at \( \theta = 90^\circ, \alpha = 90^\circ \) as
\[
S(90^\circ, 90^\circ) = \frac{n(g)\xi I Q(jk)}{4\pi \sigma(1 - p/3)} - \frac{G_0 f(P_2, \bar{P}_m)\xi I Q(jk)}{kT4\pi \sigma(1 - p/3)} - \frac{Kf(P_2, \bar{P}_m)\xi I Q(jk)}{T(1 - p/3)} \tag{2-68}
\]

where \[
K = \frac{G_0}{k4\pi \sigma} \tag{2-69}
\]

Note that \( K \) is dependent only upon the geometry of the system.
CHAPTER III: EXPERIMENTAL SETUP

In this work, a crossed-beam apparatus was used to establish the picture of the electron-atom collision. Cross sections of the V.U.V emissions were measured by normalizing the original data to the well known \( H_2 \) Lyman \( \alpha \) cross section. Figure 3-1 shows the schematic of the experimental setup. Basically, the apparatus consists of four individual systems: Vacuum system, Gas handling system, Electron beam control system, and Photon detecting system. Each system has its own components which will be discussed in detail in this chapter.

3.1 VACUUM SYSTEM

Three oil diffusion pumps were employed to pump down the main chamber, monochromator chamber, and photon detector chamber. One rotary pump was used to pump forelines of these diffusion pumps. All the pumps were made by Edward High Vacuum LTD, Sussex, England.

The main chamber was evacuated by a 6 inch water cooled oil diffusion pump with a cold trap maintained at \(-100^\circ\) C by a Cryocool CC-100 heat exchanger charged with Freon 11. A vacuum of \( 10^{-7} \) torr could be easily obtained by continuously pumping for 10 hours after a gas change. For the monochromator, a similar pumping system was used.

The photon detector chamber was pumped by a 2 inch water cooled oil diffusion pump which enabled a vacuum of \( 10^{-6} \) torr to be obtained.
FIGURE 3-1: Block diagram of the experimental setup
Instead of a cold trap, here a thermo-electrically cooled baffle was used to prevent oil from back streaming. The rotary pump had a pumping speed of 44 m$^3$ per hour. Typical backing pressure was 10$^{-2}$ torr.

The main chamber and photon detector chamber were made from non-magnetic stainless steel. And the main chamber was constructed with 9 ports. The axes of the 8 ports have a common intersection point (center of the collision region). Six of the ports are mutually orthogonal, while two others are oriented at an angle such that the monochromator can be operated at the "magic angle" which allows the elimination of the instrumental polarization correction in the cross section measurement. The remaining port was used for an ionization gauge.

3.2 GAS HANDLING SYSTEM

High purity gases (>99.95%) were used in the experiment. In order to attain a highly collimated steady gas beam, which would provide a constant gas number density in the collision region, a convenient gas handling system was built for this purpose. Figure 3-2 gives the schematic of this system. All the gas lines were made of stainless steel tubing joined by Swagelok fittings except the copper tubing between the gas cylinder and the entrance valve to the gas reservoir which was kept at high pressure of 3 atmospheres monitored by a capsule dial gauge. With this high pressure in the gas reservoir, a steady gas beam could be provided through a needle valve and a capillary nozzle. The components of the system were carefully cleaned prior to assembly and tested for leaks after assembly. When the chamber was opened for
FIGURE 3-2: Gas handling system
maintenance, the system was baked thoroughly in order to remove any desorbed gases inside, especially water vapor <18>. In most cases, the gas beam was operated under molecular flow conditions. For each gas, the pressure limit for molecular flow varies, and the plot of the intensity of a certain spectral line versus gas pressure could indicate the pressure region for molecular flow. The gas pressure was accurately determined by a capacitance manometer. This instrument had a quoted accuracy of 1% . However, the comparison with a more recently calibrated instrument from another laboratory suggested that our instrument was probably 2-3% lower in its pressure readings for the pressure higher than 100 mT. Since our calibration technique depended only on the signal comparisons from two gases at the same normal (not necessarily absolute) pressure, this slight inaccuracy in the absolute pressure measurement was not significant.

3.3 ELECTRON BEAM

This system includes the electron source, the focusing and accelerating lenses, and the electron collector. Figure 3-3 shows the arrangement of the electron gun, collision region and the electron collector (Faraday Cup).

Electrons from a thoriated tungsten filament are focused and accelerated by a series of lenses to form a fine electron beam passing through the collision region. The whole electron gun is mounted on a copper housing
FIGURE 3-3: Schematic of the electron gun and faraday cup.
which can be easily removed for cleaning. The Faraday Cup current is measured by a picoammeter. Figure 3-4 gives the control circuitry used in this experiment.

The collision region was operated at ground potential to avoid any external fields due to the grounded vacuum chamber and electron gun mount. The filament was kept at -V volts, while eV was the required electron energy.

The electron beam current was normally between 20-130 μA. Figure 3-5 gives a typical example of the variation of photon intensity versus electron current. It is clear that the intensity of a spectral line is linearly proportional to the electron current thus demonstrating the absence of secondary effects involving the electron current.

Studies of the threshold behaviors for the simultaneous ionization and excitation of Ar⁺ 92.0 nm indicated that the electron beam had an energy spread of Full Width at Half Maximum (FWHM) 1.0 eV at energy around 30 eV and current 40 μA. The electron energy was calibrated by performing the threshold excitation of several atomic lines with known onset energies. Typical contact potential of the electron beam was found to be 5 eV, although it increased slightly with running time <19>.

3.4 PHOTON DETECTING SYSTEM

This system is composed of three parts: a VUV spectrometer, a channel electron multiplier and a standard counting system.
FIGURE 3-4: Electron gun circuit diagram.
**FIGURE 3-5:** Intensity variation with electron current for the FI 95.5 nm from $e + CF_3H$
MONOCHROMATOR

This was a McPherson half meter Seya-Namioka VUV spectrometer. A gold-coated concave grating blazed at 70 nm with 1200 grooves per millimeter and linear reciprocal dispersion 1.7 nm per millimeter at the exit slit was set on a base that could be rotated about a vertical axis through its center. A synchronous stepping motor driven by a programmable control unit controlled the rate of grating rotation (wavelength scanning), see Figure 3-6. A manual control permitted the necessary precise wavelength setting when a certain spectral line was measured. The spectrometer was designed to focus the image of the entrance slit onto the exit slit with unit magnification.

Since the efficiency of the spectrometer was heavily dependent upon the grating coating <20>, we cleaned the grating regularly and always kept a high vacuum of $10^{-7}$ in the chamber to minimize the contamination due to the oil vapor from the pumping system.

PHOTON DETECTOR

A mullard 419 BL channel electron multiplier (CEM) was used to detect the photons at the exit slit of the monochromator. This detector had a high signal to noise ratio. And it was very quiet; generally, noise counts were 2-3 per minute. In order to achieve high statistical accuracy, a measurement was made for several days, even for weeks when it was necessary.
FIGURE 3-6: Schematic of the control system for automatic wavelength scans.
PULSE COUNTING SYSTEM

A standard pulse counting system was used to process the pulses produced from the channel electron multiplier. This system had a sensitive preamplifier, a delay line amplifier, a discriminator, a timer, and a pulse counter (when a single spectral line was measured) or a multichannel analyzer (for the case that a spectrum was required).

In order to make automatic measurements of an excitation function, a ramp could be used to vary the electron energy. This ramp was connected to the multichannel analyzer (see Figure 3-7 for the schematic) such that each channel in the MCA corresponded to a certain unique energy.

With this apparatus, two typical measurements can be made. One is the measurement of the excitation function of a single spectral line. In this case, the grating is set at the appropriate position for the wavelength to be studied, and the electron energy is changed either automatically by a ramp or manually by the experimenter. Alternatively, a wavelength scan can be made. Here, the electron energy is fixed, and the grating is rotated by the stepping motor. The control unit automatically controls the dwell time of the MCA and the stepping speed of the motor, as well as the number of scans desired.
FIGURE 3-7: Schematic of the control system for excitation function measurement.
CHAPTER IV: CALIBRATION OF THE VUV PHOTON DETECTION SYSTEM

4.1 INTRODUCTION

In the studies of excitation processes by means of emitted photons, the absolute calibration of the optical equipment has always been a major problem. This is especially so when the photon intensity measurements are performed in the vacuum ultra-violet (VUV) region. So far, many techniques for the calibration of the optical apparatus have been developed and used in various laboratories. Each technique has its own advantages and disadvantages, and the wavelength range covered by the calibration depends on the particular technique to be used. Some of the techniques are simply not convenient to use.

Basically, two types of techniques are used to approach the calibration of the optical system. One of them is to employ a standard light source or detector to calibrate the VUV spectrometer. Examples are the use of photodiode detectors as transfer standards <21-22>, or the use of synchrotron radiation as a standard light source <23>. Deuterium lamps <24>, argon miniarcs <25-26>, and well stabilized hydrogen arcs <27-28> have also been used as standard light sources. However, most of these sources are not generally available, and are not convenient to use. The other calibration technique is to use VUV radiation following electron impact on atoms and molecules as a secondary standard <29-30>. This technique will be discussed in detail later in this chapter. The molecular branching ratio technique <31-33> is often used to give a relative spectral response of the optical apparatus. Some researchers use a dual
spectrometer technique with an uncalibrated light source for the relative efficiency determination of the optical system <34-35>, but this technique suffers from problems introduced by the polarizing effect which occurs following multiple reflections.

Because of their relative ease of use, electron impact secondary standards have been used widely. However, the applicability of this technique heavily depends upon the availability of the cross section data in the VUV region. Unfortunately, there are few well known cross sections, and the detector efficiency often varies rapidly in this spectral region. These facts present a great difficulty for the system calibration. Even so, this technique has its unique advantages since such a "same source" calibration does not need any special devices, and the geometrical factors affecting the cross section measurement cancel out. Some sources of error such as using different part of the grating, or of the detector can be avoided.

The calibration method used in this work combines the use of electron impact secondary standards with the molecular branching ratio technique. We chose the atomic hydrogen Lyman series emissions as secondary standards following electron impact on atomic hydrogen beam produced by a RF-discharge source <36>. The amount of both atomic and molecular hydrogen can be accurately measured. By using theoretical calculations of atomic hydrogen Lyman series emission cross sections following 200 eV electron impact <37> as secondary standards, we were able to calibrate the optical system at these wavelengths. The branching
ratio technique with molecular hydrogen as target gas following electron impact was then used to interpolate the calibration between the reference wavelengths.

4.2 EXPERIMENTAL DETAILS

The special feature of the experimental setup employed for the system calibration was the use of a RF-discharge source. Figures 4-1 and 4-2 give a detailed description of this source. Since other parts of the setup have been discussed in Chapter III, only the discharge source will be discussed in this section.

Several types of radio frequency discharges have been developed and used by a number of experimenters [36,38-39]. We selected the type of Slevin and Sterling [36]. This source has a high dissociation fraction for hydrogen (95%), and a beam number density of up to $10^{13}$ atoms per cubic centimeter. Figure 4-1 shows this complete source with the cylindrical vacuum tank. The discharge tube and RF cavity are schematically shown in detail in Figure 4-2.

DISCHARGE TUBE

The discharge tube is a 220 mm long, 18 mm diameter Pyrex tube surrounded by a water cooling jacket. The exit of the tube has a 1 mm inner capillary nozzle. The shape of the tube was designed such that the gas is most likely to be discharged before leaving the main tube. The water cooling jacket is used to minimize recombination of hydrogen
FIGURE 4-1: Illustrated is the complete rf-discharge source including its vacuum tank and external connections.
FIGURE 4-2: Illustration of the discharge tube and rf cavity. The magnified inset shows our nozzle. It is configured differently from some previous nozzles.
atoms into molecules on the Pyrex surface of the tube \(<40\). Since the impurities on its surface can greatly increase the recombination coefficient, the tube must be cleaned thoroughly before being used \(<19\). After being cleaned, the source is mounted on the chamber, and pumped down as soon as possible to prevent re-contamination of the surface.

RF-CAVITY AND GENERATOR

The coaxial resonator cavity, 70 mm in diameter and 89 in height, consists of a 25-turn helical inner conductor. The outer part of the cavity is made from a solid piece of high conductivity oxygen free copper. The cavity is driven by an impedance matched RF generator which can deliver a maximum of 50 watts power at 35 MHz frequency.

THE WATER COOLING SYSTEM

Figure 4-3 gives a schematic of the water cooling system which is composed of two separate water lines. Distilled water is used to cool the discharge tube, and transfer the heat to a heat-exchanger from which heat is carried away by tap water. The flow rate of water through the cooling jacket is controlled by a flow sensor. If the flow rate drops too low, the RF generator, water pump and two solenoid valves are shut off automatically until the reset button is pushed. In this way, some protection is afforded if a leak in the tube should occur inside the vacuum system.
FIGURE 4-3: The water cooling system.
It has been believed that dissociation in the discharge is caused by electron impact <41>. The onset energy for hydrogen dissociation was found to be $8.8 \text{ eV} = 0.2 \text{ eV}$, which is the excitation energy from the ground state $H_2^1\Sigma_g^+$ to the lowest repulsive state $H_2^3\Sigma_u^+$ with production of two ground state atoms. The next higher state $H_2^3\Sigma_g^+$ with an excitation energy $11.8 \text{ eV}$ could cause dissociation by decaying to the repulsive state $H_2^3\Sigma_u^+$. The potential curves for these states are shown in Figure 4-4. During the dissociation, the excited atoms are expected to exist, but they have no contribution to the intensity measurement because of the immediate radiation inside the tube rather than at the collision region. Application of an electric field of sufficient strength to quench any metastable $2s$ atoms yielded no observable signal at the detector. In the absence of electronically excited species, we assume that the target is totally dominated by ground state atoms and molecules.

4.3 THE OPERATIONAL CHARACTERISTICS OF THE SOURCE

CONSTANT MASS FLOW

The source is operated such that the mass flow through the discharge source is constant when the discharge is either on or off. Mathematically this can be expressed as:

$$F(H_2) = \sum_n F'(H, n) + \sum_{\nu} F'(H_2, \nu) \quad (4-1)$$
FIGURE 4-4: $H_2$ potential energy curves.
Where $F(H_2)$ is the mass flow of molecular hydrogen into the discharge source. $F'(H,n)$ is the mass flow of atomic hydrogen in the $n$th electronic level out of the source, while $F'(H_2,v)$ is the mass flow of molecular hydrogen in the $v$th vibrational level out of the source. The total mass flow of $H_2$ into the discharge source is equal to the sum of atomic and molecular hydrogen mass flow at all levels out of the source. Since no evidence of excited atomic hydrogen and vibrationally excited molecular hydrogen has been observed $<36,42>$, Equation 4-1 can be simplified as

$$F(H_2) = F'(H) + F'(H_2) \quad (4-2)$$

where $F'(H)$ is the mass flow rate for H(1s) atoms out of the discharge source, and $F'(H_2)$ is the mass flow rate for ground state $H_2$ molecules out of the source.

DISSOCIATION FRACTION

The dissociation fraction is a very important parameter in the discharge experiment. It is defined as the ratio of the mass flow rate of atomic hydrogen out of the system to that of the molecular hydrogen flowing into the system (i.e., the total mass flow rate out of the system).
\[ D = \frac{F'(H)}{F(H_2)} \]

from (4-2)

\[ = \frac{F(H_2) - F'(H_2)}{F(H_2)} = 1 - A \quad (4-3) \]

where

\[ A = \frac{F'(H_2)}{F(H_1)} \quad (4-3b) \]

where \( A \) is the fraction of molecular hydrogen after discharge. The mass flow rate \( F \) can be written as:

\[ F = n m v A \quad (4-5a) \]

since \( v \propto \sqrt{T/m} \)

\[ = c n \sqrt{T/m} \quad (4-5b) \]

or

\[ n = \frac{F}{c \sqrt{T/m}} \quad (4-6) \]

where \( n \) is the number density of target atoms, \( m \) is the mass of the atom, \( a \) is the cross sectional area of the tube, and \( v \) is the flow velocity. To determine \( D \), we make two measurements. First, we carefully choose a range of molecular hydrogen emissions excited by an electron beam, and set the monochromator for this wavelength range by appropriately selecting the wavelength and the widths of both entrance and exit slits. Then, we detect the molecular emissions with discharge first on then off. We express the detected signals as

**Discharge off**

\[ S(H_2) = G n(H_2) Q(H_2) \]

from (4-5)

\[ - \frac{B F(H_2) Q(H_2)}{\sqrt{T m(H_2)}} \quad (4-7) \]

**Discharge on**

\[ S'(H_2) = \frac{B F'(H_2) Q(H_2)}{\sqrt{T' m(H_2)}} \quad (4-8) \]
where G and B are constants which are dependent upon the geometry of
the system. \( m(H_2) \) is the mass of molecular hydrogen, and \( Q(H_2) \) is the
total apparent excitation cross section. Taking the ratio of Equations
(4-7) and (4-8) gives

\[
\frac{S'(H_2)}{S(H_2)} = \frac{F'(H_2)}{F(H_2)} \sqrt{\frac{T}{T'}}
\]

from (4-3)

\[
= (1 - D) \sqrt{\frac{T}{T'}}.
\]

for \( T = T' \)

\[
= 1 - D
\]  

(4-9)

In the last step in Equation (4-9), we used the equality of \( T \) and \( T' \);
since the kinetic temperatures \( T \) and \( T' \) with discharge on and off are
the same <42>.

4.4 TRAPPING EFFECT OF RESONANCE RADIATIONS

Trapping effect of resonance radiations is one of the major problems in
the absolute intensity measurement of VUV emission. For some emissions
such as Ar 104.8 nm, this effect is very strong (see Figure 4-5 for
example), and it turns out to be a major source of uncertainty in the
determination of its emission cross section. For some other emissions
such as \( \text{Ar}^- \) 92.0 nm, this effect is negligible because of the low density
of ions in the target region. Trapping effect can be controlled to some
extent by reducing the gas flow rate into the system (using a relatively
small diameter nozzle, for example), or by keeping a high vacuum in the
chamber (enhancing the pumping speed, for example). Figure 4-5 shows
FIGURE 4-5: Intensity variation with gas pressure for Ar 104.8 nm emission following 200 eV electron impact by using • - Rectangular nozzle, ▲ - Single capillary, □ - Discharge source, • - single needle, × - Multi-capillary nozzle.
the curves of the intensity versus gas pressure for Ar 104.8 nm emission by using different nozzles. The trapping effect is most serious for the case of the rectangular nozzle which has a cross sectional area much larger than that of the single capillary nozzle. In order to correct for the trapping effect, we define a trapping factor $A(P)$ to describe the fraction of radiation being trapped en route from the collision region to the detector.

$$A(P) = \frac{S(P)}{S_0(P)}$$

$$= \exp\left(-\alpha \int_0^L n(P, x)dx\right) \quad (4-10a)$$

when trapping is small \hspace{1cm} = 1 - \alpha \int_0^L n(P, x)dx \quad (4-10b)$$

Where $S(P)$ is the signal observed at gas pressure $P$, while $S_0(P)$ is the signal that would be observed in the absence of any trapping at a gas pressure $P$. $n(P, x)$ is the number density of the absorbers at a distance $x$ to the collision region. $L$ is the effective length of the absorption path. When the absorption is small, the factor $\alpha$ in Equation (4-10) is given by <44>:

$$\alpha = cf\lambda \sqrt{\frac{M}{T}} \quad (4-11)$$

where $c$ is a constant, $\lambda$ and $f$ are the wavelength and optical oscillator strength of the transition in question, $M$ is the molecular weight of the
gas studied, and T is the absolute temperature. Note that n(P,x) is a function of the gas pressure at the position x, thus it can be written as

\[ n(P,x) = \beta f(P)g(x) \]  \hspace{1cm} (4-12)

where \( f(P) \) is a function of the gas pressure, \( g(x) \) is a geometric factor, \( \beta \) is a constant. Substituting Equation (4-12) in (4-10a) gives

\[
A(P) = \exp\left(-\alpha \beta f(P) \int_0^x g(x) dx\right)
\]

\[
= \exp[-\alpha \beta f(P) G(L)]
\]

\[
= \exp[-\epsilon f(P)]
\]  \hspace{1cm} (4-13)

where

\[
\epsilon = \alpha \beta G(L)
\]  \hspace{1cm} (4-14)

Using Equations (4-10) and (4-14), we can determine \( A(P) \) and \( \epsilon \) by doing intensity-gas pressure curve fitting. From Equations (4-11) and (4-14), we know that constants \( c, \beta \) and \( G(L) \) are the same for all Lyman series lines, and we can calculate these trapping factors by measuring only one emission line, Lyman \( \alpha \) for example. For atomic hydrogen, the number density after discharge from Equation (4-6) is given by

\[
n(H) = \frac{F'(H)}{c \sqrt{m_H T}}
\]

\[
from \hspace{1cm} (4-3)
\]

\[
= \sqrt{2} DF(H_2) \frac{c \sqrt{m_H T}}{c \sqrt{m_H T}}
\]

\[
= \sqrt{2} Dn(H_2)
\]  \hspace{1cm} (4-15)

i.e., from (4-12)

\[
f^\prime(H) = \sqrt{2} Df_{H_2}(P)
\]  \hspace{1cm} (4-16)
where \( m_n \) is the mass of atomic hydrogen, \( m_{H_2} \) is the mass of molecular hydrogen, \( n(H_2) \) is the number density of molecular hydrogen before discharge, \( f_H(P) \) and \( f_{H_2}(P) \) are the pressure functions for atomic and molecular hydrogens respectively, and \( D \) is the dissociation fraction of hydrogen molecules under the discharge. Substituting the above equation in (4-10) gives a trapping factor for atomic hydrogen emission in terms of molecular hydrogen pressure function \( f_{H_2}(P) \) as

\[
A(P) = \exp[-\alpha\beta\sqrt{2Df_{H_2}(P)G(L)}]
\]

(4-17)

\( f_{H_2}(P) \) can be determined experimentally from the curves of photon intensity versus gas pressure with discharge off for molecular hydrogen. In Figure 4-6, we show the plot of the intensity for atomic hydrogen Lyman \( \alpha \) emission versus \( f_H(P) \) i.e., \( \sqrt{2Df_{H_2}(P)} \). Define a parameter \( \gamma \) as

\[
\gamma = \frac{\alpha'}{\alpha_0} = \frac{f'\lambda'}{f_0\lambda_0}
\]

(4-18)

where \( f_0 \) and \( \lambda_0 \) are the optical oscillator strength and wavelength for atomic hydrogen Lyman \( \alpha \). The prime terms refer to the other lines of the series. Using the Equation (4-18), we are able to calculate the trapping coefficient \( \gamma \) of other lines of Lyman series by comparison with that of Lyman \( \alpha \). When the discharge is turned on, the signal of Lyman series emissions from electron impact on atomic hydrogen is given by
FIGURE 4-6: Emission rate of H Lyman $\alpha$ versus $\sqrt{2} D f_{H_2}(P)$ (mTorr) (proportional to H number density, see text).
where \( S^\text{on} \) and \( S^\text{off} \) are the signals with discharge on and off respectively under the constant mass flow condition. Figure 4-7 shows the plots of \( S_r \), \( S^\text{on} \) and \( S^\text{off} \) for the discharge source as a function of wavelength.

4.5 CROSS SECTION EXPRESSION

It is very important to correct for any polarization effects in the cross section evaluation. Since our measurements were made at a right angle to both gas beam and electron beam, the polarization effect did come into the signals observed with a correcting factor \((1-p/3)\). However, this effect is very small (less than 4\%) in our measurement since the electron energy used was 200 eV. Taking into account all the factors discussed above, we get an expression for the emission cross section of a particular spectral line as

\[
\sigma = \frac{S(1-p/3)}{Kf(P)I\eta A(P)\xi} \tag{4-20}
\]

where \( S \) is the signal, \( K \) is the geometrical factor, \( I \) is the electron current, \( \eta \) is the sensitivity of the detector, \( \xi \) is the instrumental polarization sensitivity of the system, \( f(P) \) is the pressure function given by Equation (2-61), and \( A(P) \) is the trapping factor given
FIGURE 4-7: $H_2$ spectra at 200 eV energy and 0.28 nm resolution
(a) discharge off (b) discharge on (c) atomic H lines.
by Equation (4-13). If we express the reference spectral line by \( r \) (reference), and the unknown line by \( u \) (unknown), and take the cross section ratio of these two lines, we obtain

\[
\frac{\sigma_u}{\sigma_r} = \frac{S_u(3-p_u)\alpha_r(P_r)\alpha_r(P_r)\eta_r I_r \xi_r}{S_r(3-p_r)\alpha_u(P_u)\alpha_u(P_u)\eta_u I_u \xi_u} \tag{4-21}
\]

If we set the reference line to be one of the Lyman series from electron and atomic hydrogen collision, and use Equation (4-19), \( S_r = S^{on} - (1-D)S^{off} \), Equation (4-21) becomes

\[
\frac{\sigma_u}{\sigma_r} = \frac{S_u(3-p_u)\alpha_r(P_r)\alpha_r(P_r)\eta_r I_r \xi_r}{[S_u^{on} - (1-D)S_u^{off}](3-p_r)\alpha_u(P_u)\alpha_u(P_u)\eta_u I_u \xi_u} \tag{4-22}
\]

The above equation can be simplified in our case. First, the polarizations in the case of 200 eV electron impact are less than 4%, thus can be dropped without causing significant error. Since we are always dealing with essentially unpolarized radiation, the instrumental polarization sensitivity cancels out (\( \xi_u = \xi_r \)) from Equation (2-40d). We kept electron current constant (\( I_u = I_r \)) in the measurement for both unknown and reference lines. The unknown line is also one of the Lyman series, so that \( f_u(P_u) = f_r(P_r) \). Taking the efficiency \( \eta_r \) of the reference line as unity, we re-write Equation (4-22) as
\[
\frac{\sigma_u}{\sigma_r} = \frac{(S^m_u - (1-D)S'^{eff}_u)A_r(P_r)}{(S^m_r - (1-D)S'^{eff}_r)\eta_u A_u(P_u)}
\]

or

\[
\eta_u = \frac{(S^m_u - (1-D)S'^{eff}_u)\sigma_r A_r(P_r)}{(S^m_r - (1-D)S'^{eff}_r)\sigma_u A_u(P_u)}
\]

\[
\text{from (4-11, 17, 18)} = \frac{(S^m_u - (1-D)S'^{eff}_u)\sigma_r}{(S^m_r - (1-D)S'^{eff}_r)\sigma_u} \exp\left[-\sqrt{2} DF_{H_2}(P_{H_2})\alpha_r(1-\gamma_u)\right]
\]

(4-24)

where \(\sigma_u\) and \(\sigma_r\) are the apparent emission cross sections of the atomic hydrogen Lyman series lines, and \(\gamma_u\) is the trapping coefficient of the unknown emission given by Equation (4-18).

The dissociation fraction defined by Equation (4-9) was obtained by detecting the molecular emissions \(S(H_2)\) and \(S'(H_2)\) far away from the Lyman series lines with discharge on and off respectively under otherwise the same operational conditions. Usually, our dissociation fraction had a value of 65% or higher. Since our efficiency calibration depends upon the comparison of two spectral lines from atomic hydrogen with the Lyman \(\alpha\) as a unit calibration point, the experimental conditions for exciting both lines must be identical. Instead of measuring the individual emissions of \(H\) Lyman series, we run two types of spectral scans with discharge on and off over a wavelength range of 90–130 nm which includes the Lyman series. The spectra are named \(S^m\) (signal with discharge on), \(S'^{eff}\) (signal with discharge off), and are shown in Figure 4-7. From Equation (4-19), we get our atomic hydrogen Lyman series emissions \(S_r\) by subtracting the normalized spectrum \((1-D)S'^{eff}\) from the spectrum \(S^m\) (see Figure 4-7). The efficiency calibration values are listed in Table 4-1.
TABLE 4-1
Atomic Hydrogen Line Emission Parameters

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>$Q_{\text{ext}}$</th>
<th>$Q_{\text{em}}$</th>
<th>Branching Ratio</th>
<th>Cascade %</th>
<th>Relative Efficiencies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lyman α 121.6</td>
<td>41.6</td>
<td>43</td>
<td>1.0000</td>
<td>3.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Lyman β 102.6</td>
<td>7.10</td>
<td>6.45</td>
<td>0.8816</td>
<td>3.1</td>
<td>2.76</td>
</tr>
<tr>
<td>Lyman γ 97.3</td>
<td>2.52</td>
<td>2.15</td>
<td>0.8390</td>
<td>1.9</td>
<td>3.60</td>
</tr>
<tr>
<td>Lyman δ 95.0</td>
<td>1.20</td>
<td>0.99</td>
<td>0.8177</td>
<td>0.9</td>
<td>3.50</td>
</tr>
<tr>
<td>Lyman ε 93.8</td>
<td>0.66</td>
<td>0.53</td>
<td>0.8053</td>
<td>0.0</td>
<td>4.12</td>
</tr>
</tbody>
</table>

(a) The unit of these cross section data is $10^{-18}\text{cm}^2$ at 200 eV energy.
(b) Errors in these data are below 6% added in quadrature.
Uncertainties in cross sections are not included.
The branching ratio (B's) and cascade percentage (C's) have been calculated using Einstein A coefficients published by the National Bureau of Standards <45>. They relate to the total cross section by the following relation

\[ \sigma_{app} = \sigma_{tot} B (1 + C\%) \]  \hspace{1cm} (25)

The total cross sections for the Lyman series from electron impact on atomic hydrogen are taken from Vainstein <37>, and are shown in Table 4-1 for 200 eV electron impact.

4.6 BRANCHING RATIO TECHNIQUE

The atomic hydrogen Lyman series provides us with some relative detection efficiency values at various wavelengths from 93.8 nm to 121.6 nm. However, as mentioned above, the spectral response of the detector to the VUV emissions in this region changes rapidly. We can not depend on a detection efficiency curve over 40 nm range with only five calibration points. To obtain additional calibration points, we use the molecular branching ratio technique <31-33> with molecular hydrogen as target gas. The useful information for the establishment of the molecular hydrogen synthetic spectrum covering all the Rydberg transitions in this region are the transition probabilities, oscillator strengths, Frank-Condon factors, and the excitation cross sections. We used the published values for all these parameters <46-51>. Since our experimental spectra were taken with equal entrance and exit slits, we modelled the
instrumental resolution for the synthetic spectra by a triangular slit function. Figure 4-8 gives a synthetic $H_2$ spectrum with a resolution of 0.28 nm together with an experimental $H_2$ spectrum in the same range and same resolution.

When the synthetic spectrum is set up, we divide the spectrum into certain number of features that show up over the wavelength range under consideration. Each spectral feature gives a single calibration point by taking the intensity ratio of the experimental spectrum to the corresponding synthetic spectrum. When all the calibration points are normalized to unity at the Lyman $\alpha$ wavelength 121.6 nm. Figure 4-9 gives the curve of our relative detection efficiency of the system. Note that the branching ratio calibration points are in good agreement with the points obtained at the various atomic hydrogen Lyman series emissions.

The branching ratio technique has been widely used. Figure 4-10 shows the $H_2$ synthetic spectrum obtained by Ajello, Shemansky, and co-workers <46,49,52,53>. As a comparison, our synthetic spectrum is also shown in the same figure. Figure 4-11 gives the relative efficiency curve obtained with their synthetic spectrum. The two curves are in good agreement within 10%.
**FIGURE 4-8**: $H_2$ spectra with 0.28 nm resolution and 200 eV electron energy. (a) Experimental spectrum corrected for detector sensitivity (b) our synthetic spectrum.
FIGURE 4-9: Our relative efficiency curve. • obtained by using the branching ratio technique. ◊ obtained from the H Lyman series.
FIGURE 4-10: $H_2$ synthetic spectrum obtained by (a) this Lab, (b) Ajello and Shemansky (see text).
FIGURE 4-11: Relative efficiency curve by using Ajello and Shemansky's $H_{2}$ synthetic spectrum (see text).
CHAPTER V: VUV SPECTROSCOPIC STUDIES OF $e + CF_3H$ COLLISION

5.1 INTRODUCTION

Fluorine-containing molecules such as $CF_3H$ and $CF_4$ are widely used chemical compounds in industry and daily life. The fragments of these molecules are chemically active and play important roles in the chemical etching of semiconductor materials [55]. Previous researches dealing with these molecules include the time of flight study of the Rydberg formation in $CF_2Cl_2$ and $CFCl_3$ following electron impact [56], and dissociative excitation of $SF_6$ [57] and $CF_4$ [58]. This work presents data on the fragmentation processes and dissociative excitation of $CF_3H$ following electron impact.

$CF_3H$ has been extensively investigated in experiments involving absorption spectroscopy [59], electron energy loss spectroscopy [60], photoelectron spectroscopy [61], photodissociation [62, 63], electron impact dissociation [64, 65] as well as in some theoretical calculations [66]. However, no work has been done on the electron impact induced emission in the VUV region below 200 nm. Generally, the emitting species in this region can be identified unambiguously, thus giving direct information about the fragmentation processes in the parent molecules. This work gives details of absolute cross section measurements of FI, FII, CI, CII, and HI emissions in the wavelength range 50–130 nm following 200 eV electron impact on $CF_3H$. The fragmentation processes have been investigated by looking at the threshold behavior of several of the stronger emission features. Excitation functions have been
determined from threshold to 600 eV electron impact energy. Comparisons are made with data obtained in the earlier experiments on $SF_4$ and $CF_4$ <57, 58>. No molecular emissions are observed in this wavelength region.

5.2 EXPERIMENTAL DETAILS

5.2.1 APPARATUS

The apparatus has been described in Chapter III, thus, only a brief description is given here. The VUV emissions were observed at right angles to a crossed- electron beam - gas beam arrangement using a half meter Seya-Namioka VUV spectrometer with a gold-coated grating blazed at 70 nm and reciprocal linear dispersion 1.7 nm/ mm. The dispersed photons were detected by a Mullard 419 BL channel electron multiplier connected to a standard pulse counting system. The electron beam current was controlled between 20–150 μA. In this region, the output signals were linearly proportional to the electron current. The gas beam was operated at a source pressure between 10 - 50 mTorr as monitored by a MKS Instruments capacitance manometer. A check was made to ensure that the emission intensity varied linearly with source pressure. No correction for polarization of the radiation was made, since previous experiments dealing with the electron impact dissociation of molecules revealed no significant polarization for all but simplest targets <57, 58>. Excitation function measurements and wavelength scans were carried out automatically. The data were stored in a multichannel analyzer (TN-1710), and were analyzed later by a computer (IBM 9001).
5.2.2 CALIBRATION PROCEDURE

The calibration of the photon detection system in the wavelength range 90-130 nm has been described in Chapter IV. This section only discusses the calibration between 50 nm - 90 nm region. Since the H\textsubscript{2} molecular branching ratio technique cannot be used in this region because of the absence of the H\textsubscript{2} molecular emissions, we employed the calibration method discussed in earlier publications <69, 70>. Basically, the known cross sections of some rare gas resonance transitions and some nitrogen ion transitions were used to establish the calibration points. Obviously, the accuracy of the calibration depends upon the reliability of the cross section data used. In the wavelength regions appropriate to the He resonance transitions around 50-60 nm and hydrogen Lyman \(\alpha\) at 120 nm, the accuracy is relatively high (10%) because of the high accuracy of the cross section data. In the other wavelength regions, the accuracy is much lower (25% or larger) because of the large uncertainties in the cross section data in these regions. Table 5-1 lists the cross sections used for the calibration, and the calibration curve is given in Figure 5-1. As can be seen, reasonable agreement between the points using different targets is obtained. However, there is clearly a need for additional calibration points in some regions. The peak near 70 nm reflects the blaze of the grating.
TABLE 5-1
CROSS SECTION DATA USED FOR NORMALIZATION OF EXCITATION FUNCTIONS

<table>
<thead>
<tr>
<th>line (nm)</th>
<th>Apparent Cross Section at 200 eV (10⁻¹⁶ cm²)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>He I 53.7</td>
<td>2.26</td>
<td>29, 30, 78</td>
</tr>
<tr>
<td>He I 58.4</td>
<td>8.57</td>
<td>29, 30, 78</td>
</tr>
<tr>
<td>N II 67.1</td>
<td>0.28</td>
<td>35</td>
</tr>
<tr>
<td>N II 74.7</td>
<td>0.17</td>
<td>35</td>
</tr>
<tr>
<td>N II 77.6</td>
<td>0.11</td>
<td>35</td>
</tr>
<tr>
<td>N II 91.6</td>
<td>0.47</td>
<td>35</td>
</tr>
<tr>
<td>Ar II 92.0</td>
<td>3.80</td>
<td>69</td>
</tr>
<tr>
<td>Ar II 93.2</td>
<td>1.96</td>
<td>69</td>
</tr>
<tr>
<td>Ar I 104.8</td>
<td>12.81</td>
<td>69</td>
</tr>
<tr>
<td>Ar I 106.7</td>
<td>5.32</td>
<td>69</td>
</tr>
<tr>
<td>H I 121.6</td>
<td>5.05</td>
<td>42</td>
</tr>
</tbody>
</table>

Cross Section at 100 eV

| Ar II 51.9-53.1 | 2.11 | 79 |
| Ar II 54.3-54.9 | 2.5  | 79 |
| Ar II 57.2-58.3 | 4.66 | 79 |
| Ar II 66.2-67.9 | 4.51 | 79 |
| Ar II 68.7-70.5 | 0.83 | 79 |
| Ar II 71.8-73.1 | 3.2  | 79 |
| Ar II 92.0      | 4.87 | 80 |
| Ar II 93.2      | 2.49 | 80 |
FIGURE 5-1: Detector efficiency curve of the system. □ - He points, × - Ar', 
points, Δ - Ar points, O - N' points, • - H₂Lyα.
Absolute cross section evaluation was based on a comparison between two emissions, one emission with known cross section was chosen as a reference ($H_2$ Lyman $\alpha$ in this work), the other was one of the emissions to be measured. If we express the reference line by $r$ (reference), and the unknown line by $u$ (unknown), and take the cross section ratio of these two lines, we get from Equation (4-21) the following

$$\frac{\sigma_u}{\sigma_r} = \frac{S_u(1-p_u/3)f_u(P_u)\lambda_r(P_r)\eta_r I_r \xi_r}{S_r(1-p_r/3)f_u(P_u)\lambda_u(P_u)\eta_u I_u \xi_u} \quad (5-1)$$

The measurement was carried out at 200 eV, where the polarization of $H_2$ Lyman $\alpha$ is less than 3%, and those lines from $CF_3H$ are expected to be unpolarized. Since the polarization correction, 1%, is much smaller than the statistical uncertainties and the reference error involved in the cross section evaluation, we can consider all the emissions to be unpolarized. Thus, the instrumental polarization sensitivities $\xi_u$ and $\xi_r$ in Equation (5-1) cancel out. The electron current was kept constant (100 $\mu A$) over the experiment, thus, $I_u$ and $I_r$ cancel out too. The trapping factors $\lambda_u(P_u)$ and $\lambda_r(P_r)$ were unity since the emissions discussed are not affected by resonance trapping. If we choose the efficiency of the resonance line as unity, we finally simplify Equation (5-1) as

$$\frac{\sigma_u}{\sigma_r} = \frac{S_u f_r(P_r)}{S_r f_u(P_u)\eta_u} \quad (5-2)$$

or

$$\sigma_u = \frac{S_u f_r(P_r)\sigma_r}{S_r f_u(P_u)\eta_u} \quad (5-3)$$
Equation (5-3) was the basic formula used in this work for the absolute cross section evaluation. The comparisons were made over a time interval as short as possible in order to minimize the effect of any fluctuations in the system. During a gas change (from $H_2$ to $CF_2H$), the system was pumped down without changing any of the experimental conditions to keep an identical operational environment for both the reference line and the unknown line. The electron gun and the photon detection system were both operated continuously. By doing so, identical experimental conditions were ensured for the comparisons. This procedure minimized any changes in the electron beam focusing or electronic system. The gas pressure for each emission was controlled carefully under molecular flow conditions by Intensity - gas pressure curve fitting. The molecular - viscous intersection pressure $\bar{P}_m$ in $f(P)$ function was determined by doing these curve fittings.

5.3 RESULTS AND DISCUSSIONS

5.3.1 SPECTRA

Figure 5-2 shows the emission spectrum in the wavelength region 50-130 nm produced by 200 eV electron impact on $CF_2H$. The spectrum has not been corrected for the sensitivity response of the detection system.
FIGURE 5-2: Emission spectrum of $CF_3H$ following 200 eV electron impact with a resolution of $5.1 \text{ Å}$.

Note the multiplying factors which have been applied to different spectral regions. The spectrum is uncorrected for variations of spectral sensitivity of the detector with wavelength.
Clearly, the spectrum is dominated by FI and HI emissions with the strongest lines at 78, 80.8, 95.5, and 97.5 nm for FI, Ly α and Ly β for HI. The carbon emissions that lie above 110 nm are so weak that the threshold behavior of the emissions could not be investigated, and the determination of the full excitation functions could not be made. All the spectral lines have been identified, and the transitions involved are listed along with the absolute emission cross sections in Tables 5-2 for FI and FII transitions, in Table 5-3 for CI and CII transitions, in Table 5-4 for HI transitions. The grotrian diagrams for FI, FII, CI and CII transitions are given in Figures 5-3,4,5,6 respectively.

It is noted that the FI emissions are different in many respects from those observed from $CF_4$ <58>. The comparable intensities of the quartet - doublet intercombination line at 97.5 nm and the doublet - doublet transition at 95.5 nm indicate a strong cascade contribution to the former line as was found in $CF_4$ <58>. The doublet - doublet transition at 95.5 nm is the strongest feature in the spectrum. All the major FI lines involve transitions of a 3s or 3d electron decaying to the ground state $1s^22s^22p^52p_{1/2,3/2}$. The other higher electron orbitals n>3 also contribute, but with much smaller cross sections. The multiplet structure of the FI transitions in the 95-98 nm region was investigated, and is shown in Figure 5-7 where a higher spectral resolution has been used. The figure also shows some members of HI Lyman series.

The FII emissions are much weaker than they are in $CF_4$ <58>, and $SF_6$ <57>. Actually, the only recognizable line in the wavelength region above
<table>
<thead>
<tr>
<th>WAVELENGTH (nm)</th>
<th>TRANSITION</th>
<th>CROSS SECTION (10^{-18} cm^2)</th>
<th>ONSET ENERGY (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FL 97.77</td>
<td>2s^22p^4(3P)3s^4P_{3/2} - g^2P_{1/2}</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>FL 97.65</td>
<td>2s^22p^4(3P)3s^4P_{5/2} - g^2P_{3/2}</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>FL 97.62</td>
<td>2s^22p^4(3P)3s^4P_{1/2} - g^2P_{1/2}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FL 97.39</td>
<td>2s^22p^4(3P)3s^4P_{3/2} - g^2P_{3/2}</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>FL 95.85</td>
<td>2s^22p^4(3P)3s^2P_{3/2} - g^2P_{1/2}</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>FL 95.55</td>
<td>2s^22p^4(3P)3s^2P_{1/2} - g^2P_{1/2}</td>
<td>9.3</td>
<td>33.0 ± 1.5</td>
</tr>
<tr>
<td>FL 95.48</td>
<td>2s^22p^4(3P)3s^2P_{3/2} - g^2P_{3/2}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FL 95.19</td>
<td>2s^22p^4(3P)3s^2P_{1/2} - g^2P_{3/2}</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>FL 80.96</td>
<td>2s^22p^4(1D)3s^2D_{3/2} - g^2P_{1/2}</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>FL 80.70</td>
<td>2s^22p^4(1D)3s^2D_{5/2} - g^2P_{1/2}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FL 79.45</td>
<td>2s^22p^4(3P)4s^4P_{3/2} - g^2P_{3/2}</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>FL 79.20</td>
<td>2s^22p^4(3P)4s^2P_{3/2,1/2} - g^2P_{3/2,1/2}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FL 78.24</td>
<td>2s^22p^4(3P)3d^22,4D - g^2P_*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FL 78.04</td>
<td>2s^22p^4(3P)3d^2P_{2,4D} - g^2P_*</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>FL 77.94</td>
<td>2s^22p^4(3P)3d^2P_{2,4D} - g^2P_*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FL 75.1</td>
<td>2s^22p^4(3P)4d^22,4P, 2,4D, 2,4F - g^2P_*</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5s^2,4P - g^2P_*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FL 71.1 - 73.6</td>
<td>various excited states - g^2P_*</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>FL 60.7</td>
<td>2s^2p^5 3P_{2,10} - g^3P_{1/2}</td>
<td>0.17</td>
<td></td>
</tr>
</tbody>
</table>

* Error involved in these cross sections is estimated to be 20% for those transitions with a wavelength above 90 nm, and 30% for those transitions below 90 nm.
TABLE 5-3

ABSOLUTE CI AND CII EMISSION CROSS SECTIONS
FOLLOWING 200 eV ELECTRON IMPACT ON CF₃H

<table>
<thead>
<tr>
<th>WAVELENGTH (nm)</th>
<th>TRANSITION</th>
<th>CROSS SECTION * (10⁻¹⁶ cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl 114.0</td>
<td>²s²²p²(²P₀) ³d³P₀, ¹3D₀, 1,3F₀ - ³P - ³P</td>
<td>0.20</td>
</tr>
<tr>
<td>Cl 118.3</td>
<td>²s²²p²(²P₀) ⁴d¹3P₀, ¹3D₀, 1,3P₀ - ³P - ³P</td>
<td>0.78</td>
</tr>
<tr>
<td>Cl 126.1</td>
<td>²s²²p²(²P₀)³d³P₀ - ³P</td>
<td>0.28</td>
</tr>
<tr>
<td>Cl 127.7</td>
<td>²s²²p²(²P₀)³d³P₀, ¹3F₀ - ³P</td>
<td>1.9</td>
</tr>
<tr>
<td>CII 68.7</td>
<td>²s²(¹S)³d²D - ²P₀</td>
<td>0.12</td>
</tr>
<tr>
<td>CII 85.8</td>
<td>²s²(¹S)³s²S - ²P₀</td>
<td>0.20</td>
</tr>
<tr>
<td>CII 90.4</td>
<td>²s²²p²²P - ²P₀</td>
<td>0.58</td>
</tr>
<tr>
<td>CII 103.7</td>
<td>²s²²p²²S - ²P₀</td>
<td>0.44</td>
</tr>
</tbody>
</table>

* Error in these cross sections is large (35%) because of the low intensity of the emissions.
### Table 5-4

**Absolute Hydrogen Emission Cross Sections Following 200 eV Electron Impact on CF$_3$H**

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Transition</th>
<th>Cross Section ($10^{-19} \text{cm}^2$)</th>
<th>Onset Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>121.6</td>
<td>Lyman α</td>
<td>27.1 ± 11%</td>
<td>18.4 ± 1.5</td>
</tr>
<tr>
<td>102.6</td>
<td>Lyman β</td>
<td>6.5 ± 14%</td>
<td>34.0 ± 1.5</td>
</tr>
<tr>
<td>97.25</td>
<td>Lyman γ *</td>
<td>2.7 ± 26%</td>
<td></td>
</tr>
<tr>
<td>94.97</td>
<td>Lyman δ</td>
<td>1.6 ± 18%</td>
<td></td>
</tr>
<tr>
<td>93.78</td>
<td>Lyman ε</td>
<td>1.2 ± 18%</td>
<td></td>
</tr>
<tr>
<td>91.46-93.07</td>
<td>Other Lyman lines</td>
<td>1.0 ± 18%</td>
<td></td>
</tr>
</tbody>
</table>

* Increased error due to blending of Ly α with 97.5 nm F transition
FIGURE 5-3: FI Grotrian diagram.
FIGURE 5-4: HII Grotrian diagram. Only HII 60.7 nm feature is strong enough to be measured.
FIGURE 5-5: CI Grotrian diagram.
FIGURE 5-6: CII Grottrian diagram. The transitions above 130 nm are not measured in this work.
FIGURE 5-7: High resolution spectrum of $CF_3H$ at 200 eV impact energy in the 95-98 nm spectral region. Note the presence of Ly\text{v} and $\delta$ at 97.25 nm and 94.97 nm respectively.
50 nm is FII 60.7 nm line. Such a low intensity made it impossible to study the threshold behavior of the emission or its detailed excitation function.

The HI emissions are strong as expected. Since the Ly α line was relatively intense and well isolated from other lines, we were able to study it in detail. By direct comparison of it with Ly α from H₂ excited under identical conditions, we were able to obtain a rather accurate absolute emission cross section for this line.

For CI emissions, the triplet – triplet transitions dominate the spectrum often with quite highly excited electron orbitals involved. For example, the CI line at 114 nm is due to transitions from n=7 (7s) and n=6 (6d) to the ground state. Singlet – triplet intercombination lines may also be contributing to the observed features (see Table 5-3). Use of a grating blazed for this higher wavelength region coupled with the use of a CsI coating on the detector surface would allow these transitions to be studied in greater detail than was possible in the present work.

Only doublet – doublet transitions are observed in the CII spectrum. It is found that the one electron process of inner shell ionization of a 2s electron leading to an excited ion state results in the strongest emissions at 90.4 nm and 103.7 nm. The simultaneous ionization of a 2p electron and excitation of another is much less probable. We also note that the strongest FII emission at 60.7 nm also involves removal of an inner shell 2s electron. All of this is very similar to what was observed when using CF₄ as target.
5.3.2 EXCITATION FUNCTIONS AND ABSOLUTE CROSS SECTIONS

a. FLUORINE EMISSIONS

The strongest fluorine emissions all involve excited 3s orbitals (see Table 5-2). The excitation function for the strongest feature at 95.5 nm has been measured from threshold to 600 eV electron impact energy, and is shown in Figure 5-9. The shape of the excitation function is found to be identical to that in CF₄ <58>. The values of the absolute emission cross sections of FI and FII emissions are given in Table 5-2. A low spectral resolution of 0.51 nm was used in the normalization procedure to obtain high statistical accuracy. Cross sections for the individual components of the emission feature centered at 97.5 nm and 95.5 nm were obtained from high resolution spectra (see Figure 5-7).

As discussed earlier, FII emissions from singly ionized fluorine atoms are extremely weak in the VUV region and thus could not be studied in detail. No indication of FIII emissions was found in this work.

b. CARBON EMISSIONS

Emissions from either excited neutral or singly ionized carbon atoms were too weak to be studied in detail using present detection system. Table 5-3 gives the absolute emission cross sections of CI and CII emissions at 200 eV electron impact energy. No emissions from molecular fragments involving carbon were observed in our VUV spectral region.
FIGURE 5-8: Excitation function of FI 95.5 nm emission feature.
c. HYDROGEN EMISSIONS

The hydrogen Lyman series was strongly excited (see Figure 5-2). Figure 5-8 shows the excitation function of Ly α up to 600 eV. The Fano plot of the excitation function gives a straight line at high energy which indicates an optically allowed transition in the parent molecule. This is in agreement with the observation of Van Sprang et al. <64> who studied the Balmer emission following dissociative excitation of the same parent molecule. The maximum of the cross section was found to occur around 150 eV, which was slightly higher than what was observed by Van Sprang et al <64> for Balmer series lines.

5.3.3 THRESHOLD EXCITATION

a. HYDROGEN THRESHOLD EXCITATION

Figure 5-10 shows the near threshold excitation function of Ly α line. To improve the statistical significance of the data, they are presented with an energy separation of about 1 eV between data points. The energy resolution (FWHM) of the electron gun is slightly better than this.

As can be seen from the Figure, two onset features are observed at energies of 18.4 ± 1.5 and 34.0 ± 1.5 eV. This indicates that two major channels are involved in the dissociation of the parent molecule. According to Harshbarger et al. <60>, the energy required for the transition of 3e and 5α, orbitals to the 3p Rydberg orbital is 17.4 eV,
FIGURE 5-9: Excitation function of Lyα up to 600 eV.
FIGURE 5-10: Near threshold excitation function of Lyα line.
and for 3e and 5α₃ to the 3d Rydberg orbital is 19.14 eV. Thus the first onset at 18.4 eV is likely due to the dissociative excitation of parent molecule via a transition from a 3e or 5α₃ orbital. The dissociation products are expected to be CF₃ and H⁺. The process can be expressed as

\[ e + CF₃H \rightarrow CF₃ + H⁺ + e⁻ \]
\[ \rightarrow H + Lyα \]

The minimum energy for this process is 14.76 eV indicating that an excess energy of 3.64 eV is carried away by dissociation products as kinetic or internal energy. This suggests that highly repulsive Rydberg orbitals play an important role in the dissociation process. Alcock and McConkey <56> came to the same conclusion for the dissociation of CCl₂F₂ and CCl₃F yielding excited fluorine atoms, which were endowed with large kinetic energy.

Alternatively, the CF₃ molecular fragment might be also excited. This process may be represented by the following

\[ e + CF₃H \rightarrow CF₃⁺ + H⁺ + e⁻ \]
\[ \rightarrow H + Lyα \]
\[ \rightarrow CF₃ + hν \text{ (UV broad-band emission)} \]

The broad-band emission of CF₃ between 200 and 400 nm was observed by Suto and Washida <62>, and by Suto and Lee <63> following photodissociation of CF₃H and by Van Sprang et al. <64> using electron
impact dissociation. They measured an onset for the continuous emission at 17.3 eV <64> in close agreement with our measured Ly α onset given the uncertainties in the two measurements. Taking into account the energy required for the continuous emission at a wavelength 400 nm, we estimate the onset energy for process [2] to be 17.9 eV.

The second onset for Ly α emission is 34.0 ± 1.5 eV, an energy value high enough to open many dissociation channels. One possible dissociation process is the total fragmentation of the parent molecule:

\[ [3] \quad e + CF_3H \rightarrow C + 3F + H^* + e^* \]
\[ \quad \rightarrow H + Ly \alpha \]

The energy required for this process is 29.8 eV. Other processes such as

\[ [4] \quad e + CF_3H \rightarrow CF_2 + F^* + H^* + e^* \]
\[ \quad \rightarrow H + Ly \alpha \]
\[ \quad \rightarrow F + h\nu \ (VUV \ emission) \]

can not be ruled out on the basis of onset potential determinations alone. The calculated energy required for process [4] is 31.53 eV, very close to our measured second onset and also very close to our measured first onset for FI 95.5 nm emission at 33.0 ± 1.5 eV. From Tables 5-2 and 5-4, we can see that the absolute emission cross sections of Ly α and FI 95.5 nm are very similar in magnitude.
b. FLUORINE THRESHOLD EXCITATION

In a fragmentation study of \( CF_3 \), we found three clear onsets contributing to the fluorine threshold excitation. From Figure 5-11, we see that the threshold excitation of FI 95.5 nm emission is not so definite. The first onset is clear at 33.0 eV, but the energy dependence of the near threshold excitation is such that there are no clear indications for other dissociation processes. The process associated with the first onset for FI 95.5 nm emission are probably due to the total fragmentation of the parent molecule with one excited fluorine atom or partial fragmentation via process [4] as discussed above.

5.4 CONCLUSIONS

Fragmentation of \( CF_3H \) following electron impact has been investigated over the energy range from threshold to 600 eV by monitoring the VUV radiation produced from the excited fragments. Radiation from both neutral and ionic species has been observed in the wavelength range 50-130 nm and cross sections for the production of individual features have been established. FI transitions, from excited 3s orbitals to the ground state, and HI Ly \( \alpha \) dominate the spectrum. The threshold behavior of Ly \( \alpha \) emission indicates two onsets, while the threshold behavior of FI 95.5 nm emission below 80 eV shows only one clear onset,
FIGURE 5-11: Near threshold excitation function of FI 95.5 nm emission feature.
a behavior which is quite different from the triple onsets seen in $CF_4$<sup>58</sup> and double onsets in $SF_6$<sup>57</sup>. This work has been published in Canadian Journal of Physics in 1989<sup>148</sup>. Since the publication of this work, new data has appeared (Ajello et al<sup>54</sup>, 1990) on the cross sections for the Ar lines used as calibration standards in this work. If these rather than the earlier data are used to obtain the calibration curve, Figure 5-1, then some corrections to the data in Tables 5-2 to 5-4 would have to be carried out.
CHAPTER VI: CROSS SECTIONS OF KrII TRANSITIONS AT 96.5 AND 91.7 nm

6.1 INTRODUCTION

The ion transitions $ns^2np^6 ^2P_{1/2,3/2} - nsnp^6 ^2S_{1/2}$ excited by electron impact on the noble gases are of great interest from both theoretical and practical points of view. The initial excitation process involves promotion of an inner shell electron into the continuum leaving the resultant ion in an excited state. Because the ground state of the ion is a doublet, a pair of spectral lines result, for example the Kr II lines at 91.7 and 96.5 nm, or the Ar II lines at 92.0 and 93.2 nm. The ratio of the cross sections for the two transitions provides useful information about the theoretical description of the excited species $<71,72>$. The ion lines are unpolarized, since they originate in a state which is spherically symmetric and their excitation is unaffected by the trapping effect of resonance radiations because of the low density of ions in the collision region of a typical electron impact experiment.

For these reasons the lines are potentially ideal candidates for use as secondary standards in the critical vacuum ultraviolet (VUV) spectral region 90–100 nm, but unfortunately, their excitation cross sections have not yet been established with sufficient accuracy for this to be accomplished $<69,73,74>$. In Ar there is good agreement on the intensity ratio (1.86 ± 10%) of the two lines even though considerably larger disagreement exists between the various measurements of the cross section for a particular line. However, as has been pointed out by Van Zyl (private communication, 1988) the situation with the Kr II lines is
particularly bad with very significant discrepancies even in the ratio of the excitation cross sections of the two lines. The first determination of this cross section ratio was made by Luyken, de Heer and Vriens <75> who obtained a value of 1.54. Later on, van Raan <76> measured their absolute excitation cross sections at 300 eV with a ratio of 2.5. Luyken et al. <71> measured the excitation cross section of both lines combined by normalizing to van Raan's data at 300 eV. Very recently, van der Burgt (private communication, 1988) estimated a ratio of 1.22 from survey spectra taken at rather high gas pressure, using the technique and apparatus described by McPherson et al.<23>. In view of this wide spread it was felt worthwhile to make a careful measurement of the cross sections of the lines and of their intensity ratio paying particular attention to possible sources of error which might have been present in some of the earlier work. The present work gives the result of this study. The Lyman-α emission cross section from dissociative excitation of \( H_2 <42> \) was used for normalization. In the VUV spectral region of interest, the errors involved in the calibration are estimated to be less than 15\% in the absolute sensitivity of the detection system with an error in the relative sensitivity over the range 91-97 nm being much less than this.

6.2 RESULTS AND DISCUSSION

The first concern in the determination of the cross sections is the proper isolation of the spectral lines of interest. The spectral data <77> clearly show a possibility of contamination of both 96.5 nm and 91.7 nm lines by neighboring features if insufficient spectral resolution is used.
A Kr I line at 96.3 nm could contaminate the Kr II 96.5 nm line, while an unclassified Kr line at 91.8 nm could be contributing to the Kr II 91.7 nm intensity. No evaluation of the magnitude of these effects was included in any of the earlier works.

To illustrate the magnitude of spectral contamination which could occur, several emission spectra have been taken under different conditions. Figure 6-1, taken with a spectral resolution of 0.51 nm, shows no sign of contamination for the 96.5 nm line but significant overlap occurring at 91.7 nm. The spectrum with higher resolution in Figure 6-2 clearly resolves the structure near 91.7 nm but also demonstrates the weak presence of the underlying 96.3 nm neutral Kr line which was not at all evident in Figure 6-1. It is clear from Figures 6-1 and 6-2 that insufficient spectral resolution could lead to completely erroneous estimates of the measured cross sections and thus their ratio.

A related factor which could affect the measurements is the gas pressure in the target region. The measured intensities of the neutral Kr emissions will be strongly pressure-dependent in a non-linear way because of the strong trapping of this resonance radiation which occurs. The Kr ion emissions on the other hand are not affected by this effect because of the low ground state ion density. This effect is illustrated in Figure 6-3 which shows the variation of output intensity with gas pressure for the KrII 91.7 nm and KrI 94.6 nm lines. The strong self-trapping of the latter line is clearly evident. Figure 6-4 shows the spectrum taken at relatively high gas pressure. It clearly demonstrates
FIGURE 6-1: Emission spectrum of Kr following 200 eV electron impact with a spectral resolution of 0.51 nm at 70 mTorr gas pressure.
FIGURE 6-2: Emission spectrum of Kr at 200 eV electron energy with a spectral resolution of 0.17 nm and gas pressure of 45 mTorr.
FIGURE 6-3: The emission intensity versus gas pressure curves at 200 eV electron energy, o - KrII 91.7 nm line, Δ - KrI 94.6 nm doublet.
FIGURE 6-4: Emission spectrum of Kr at 200 eV electron energy with a spectral resolution of 0.17 nm and gas pressure of 170 mTorr.
the reduced intensity of the KrI lines relative to their KrII neighbors. It is evident that a relative intensity measurement of KrII lines could be significantly pressure-dependent if poor spectral resolution was employed. Clearly, if poor spectral resolution is used, it is likely that the best value for the intensity ratio will be obtained at high gas pressure where the relative effect of KrI line contributions are minimized. This explains the agreement in Table 6-1 between the results of van der Burgt and present data. Since both KrII lines originate from the same excited level 4s4p^6 2S_{1/2} the cascade population to this state should affect both lines equally. Therefore, their cross section ratio should be independent of electron impact energy, and represent the relative transition probabilities between the states involved. Measurements using different impact energies in the range 100-300 eV have confirmed this. Table 6-1 lists our result together with the previous data. The standard deviation of ten different measurements was less than 2%. The cross section ratios of Luyken et al. \cite{75} and van Raan \cite{76} are 28% and 108% larger than the present result respectively. The 12% error quoted in our result includes a possible 10% error in the relative wavelength sensitivity of our monochromator-detector combination over the range 91-97 nm.

Absolute values for the apparent excitation cross sections of the two lines were measured at a single electron energy 200eV by direct comparison of the emitted intensities with that of Ly \alpha from H\textsubscript{2} excited under the identical conditions, making use of the previously established variation of detector sensitivity with wavelength. The values obtained were \(3.4 \times 10^{-18} \text{cm}^2\) and \(2.8 \times 10^{-18} \text{cm}^2\) for the KrII 96.5 nm and 91.7 nm
<table>
<thead>
<tr>
<th>Group</th>
<th>Ratio</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Luyken et.al (1969)</td>
<td>1.54</td>
<td>Unknown</td>
</tr>
<tr>
<td>Van Raan (1973)</td>
<td>2.5</td>
<td>300</td>
</tr>
<tr>
<td>Van der Burgt (1988)</td>
<td>1.22</td>
<td>300</td>
</tr>
<tr>
<td>Present result</td>
<td>1.22 ± 12%</td>
<td>100 - 300</td>
</tr>
</tbody>
</table>
respectively. The estimated error of ±14% is the root-square addition of
the uncertainty in the relative wavelength sensitivity 10%, the statistical
uncertainty in the count rate 2%, the error in the Ly α secondary
standard 8%, and the electron current and pressure variations 2% each.
The sum of our two cross sections is 7% higher than the measurement of
the two lines combined by Luyken et al. [71], a satisfactory but possibly
fortuitous level of agreement considering the method of normalization
used by Luyken et al.

6.3 CONCLUSIONS

The cross section ratio of KrII resonance transitions at 96.5 nm and 91.7
nm excited by electron impact on Kr has been determined to be 1.22 ±
12% under single collision conditions over the energy range 100–300 eV.
Absolute apparent excitation cross sections for the two lines were
measured to be 3.4 \times 10^{-18} and 2.8 \times 10^{-18} \text{cm}^2 respectively with an error
of 14% at an incident electron energy of 200 eV. Spectral resolution and
trapping effect of resonance radiations are demonstrated to be major
problems in the experiment. Together with ArII lines at 92 and 93.2 nm
these lines can now be used with some confidence for relative spectral
calibration in the critical 90–100 nm spectral region. This work has been
CHAPTER VII: \(N_2\) R.F. DISCHARGE EXPERIMENT

7.1 INTRODUCTION

Electron - atomic nitrogen collisions have long been a challenge in electron - atom collision physics, since they play an important role in auroral phenomena in the Earth's atmosphere, terrestrial airglow and in a variety of gaseous discharge processes. However, very little data are available so far. The major problems are basically the difficulty of \(N_2\) dissociation, and unfortunately the associated fact that a large number of excited \(N_2^+\) metastable molecules are generally produced along with \(N\) atoms in any practical source. The only work on electron impact excitation of atomic nitrogen was carried out by Stone and Zipf \(\langle 81-82\rangle\) in the 1970's, using a microwave discharge source. Excited \(N_2^+\) metastable molecules were found to be present in the target gas. Their measured cross sections were far larger than those accepted today \(\langle 83\rangle\). The electron impact ionization of atomic nitrogen was investigated by Smith et al. in 1962 \(\langle 84\rangle\) using a pulsed D.C. discharge source. This was later found to produce copious quantities of excited \(N_2^+\) metastable molecules \(\langle 85\rangle\). Recently an \(N_2\) microwave discharge source was studied as a possible source of \(N\) atoms, but again, was found to be seriously contaminated by metastable species \(\langle 86\rangle\). It is thus absolutely necessary to know how the presence of metastable species influences the observed signal when a discharge source is used to produce an \(N\) beam.

It is well known that metastable \(N_2^+\) molecules have a substantial effect on discharge characteristics \(\langle 87-89\rangle\). Recently, there has been a growing
interest in electron – metastable $N_2^*$ molecule collisions. Theoretical work on electron impact ionization of metastable $N_2^*$ molecules was done some time ago by Tannen <90> and Flannery et al. <91>. An experiment to measure the electron impact ionization of metastable $N_2^*(A^3\Sigma^+_u)$ was carried out by Armentron et al. <92> using charge transfer neutralization of an $N_2^+$ ion beam by $N_2$ and NO molecules, and by Wang and Lee <93> using a powerful ArF laser to directly excite $N_2$ molecules into metastable states, followed by electron impact ionization. No work has been done on VUV emissions induced by electron impact on metastable $N_2^*$ molecules. To check out the influence of such metastable species in the target gas on the electron impact excitation of atomic nitrogen, and to make a first step towards an experiment to measure electron impact excitation of metastable $N_2^*$ molecules, the present work has been designed and carried out. Even though not much quantitative data have been obtained, some useful results have been demonstrated. This chapter presents a study of the VUV emissions following electron impact on an R.F. Discharge – processed $N_2$ beam.

7.2 EXPERIMENTAL SETUP

The apparatus used for this work has been described in Chapter III and IV in detail. One of the key items in the experimental setup is the 35 MHz, 50 W R.F. discharge source which worked well for the dissociation of $H_2$ molecules <42>. It was hoped that, by properly choosing the discharge parameters, significant dissociation of $N_2$ would also be obtained. If $N$ atoms or excited $N_2^*$ molecules are formed in significant quantities in the discharge, then it’s expected that the onsets for
various observed spectral features would be shifted to lower energies. For this reason it was imperative to use a well focused, high current electron gun with good performance at low energy. For this purpose, a magnetically focused electron gun was designed and made. The faraday cup and electron gun were assembled in two identical non-magnetic metal tubes. Six groups of coupled Helmholtz coils were distributed equally along the tubes, and produced a near uniform axial magnetic field in the crucial region where the faraday cup and electron gun were assembled (see Figure 7-1). The average magnetic field strength in this crucial region was 125 gauss with a 5% variation using 1 Ampere current. In order to get rid of the heat generated by the solenoids and the filament of the electron gun, large pieces of solid aluminum and copper were used to build a efficient channel for heat transfer to the copper flanges where cooling fans were used to carry the heat away. Under normal conditions, this electron source was capable of producing 30 μA current at 3 eV energy, and 150 μA at 10 eV electron energy.

The hooked nozzle of the discharge tube described in Chapter IV produced numerous unavoidable collisions with the wall by the molecules passing through it. Since wall collision de-excitation of metastable species could open a likely channel for reducing the N$^+_2$ metastable concentration in the target beam, or cause enhanced N atom recombination, a new discharge tube with a straight nozzle was used in the present work.

7.3 RESULTS AND DISCUSSION
FIGURE 7-1: Schematic of magnetically focused electron gun and axial field strength.
7.3.1 $C_4^* \Sigma_u^* - X \Sigma_g^*$ System

In the spectral region from 90 nm to 110 nm, many dipole-allowed band systems have been observed, such as $b \ '\Pi_u - X \ '\Sigma_g^*$, $b' \ '\Sigma_u^* - X \ '\Sigma_g^*$, $c_n \ '\Pi_u - X \ '\Sigma_g^*$, $c_4^* \ '\Sigma_u^* - X \ '\Sigma_g^*$, and $a_n \ '\Pi_u - X \ '\Sigma_g^*$ (see Figure 7-2). The emissions from these band systems are strong and usually overlapped. It is difficult to determine the contribution from each individual band. The complexity of the band mixing can be seen from a recent publication <101>. However, the $c_4^* \ '\Sigma_u^* - X \ '\Sigma_g^*$ band system is the dominant feature in this spectral region, and the (0,0) and (0,1) bands can be fairly easily isolated from neighboring bands and NI, as well as NII emissions. The discharge-processed $N_2$ as target gas introduces a significant change to the intensity pattern of this system.

Figure 7-3 shows the comparison of the emission spectrum in this wavelength region with discharge both on and off under 200 eV electron impact on nitrogen molecules. It can be seen that the relative intensity of the $c_4^*$ (0,0) band emission and the NI 120 nm emission changes dramatically when the discharge is on. The intensity change pattern for this system is given in Table 7-1. It should be mentioned that only the (0,0) and (0,1) bands can be cleanly isolated from other emissions, the rest of this system can not be separated from other contributors. If we consider the $c_4^*$ bands as the dominant contributors to all the emission features involved except for the NI and NII emissions, a rough estimation can be made of the change in the intensity pattern of the $c_4^*$ bands with discharge on and off. In Table 7-1, $c_4^*$ bands are listed as leading contributors to each emission feature, also listed are other contributors involved. Examination of Figure 7-2 indicates that a
FIGURE 7-2: Partial energy level diagram for $N_2$ within the 12–15 eV energy region of the Rydberg and Valence states.
FIGURE 7-3: VUV emissions of $N_2$ at 200 eV impact energy.
<table>
<thead>
<tr>
<th>Band $(v', v'')$</th>
<th>Wavelength (nm)</th>
<th>Intensity Change for Various Discharge Media</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(6,4)$, b$(9,0)$, b'$(16,3),(9,1)$</td>
<td>92.8</td>
<td>$+11.6%\pm10%$ $+24%\pm15%$ $+35.2%\pm10%$</td>
</tr>
<tr>
<td>$(3,2),(4,3)$, b$(6,0),(6,5)$</td>
<td>94.4</td>
<td>$+15%\pm5%$ $+12%\pm10%$ $+23%\pm10%$</td>
</tr>
<tr>
<td>$(0,0)$, b$(13,3),(3,0),(9,2),(16,4)$</td>
<td>95.8</td>
<td>$-17%\pm6%$ $-43%\pm10%$ $-36%\pm10%$</td>
</tr>
<tr>
<td>$(0,1)$</td>
<td>98.0</td>
<td>$-15%\pm5%$ $-31%\pm10%$ $-15%\pm10%$</td>
</tr>
<tr>
<td>$(3,4),(4,5)$, b$(1,0),(7,2)$</td>
<td>98.6</td>
<td>$+23%\pm5%$ $+61%\pm15%$ $+70%\pm10%$</td>
</tr>
<tr>
<td>$(5,7)$, b$(0,0),(4,1),(6,3),(9,4)$</td>
<td>98.9</td>
<td>$+28%\pm5%$ $+24%\pm15%$ $+53%\pm10%$</td>
</tr>
<tr>
<td>$(0,2),(1,3)$, c$(2,4)$</td>
<td>100.3</td>
<td>$+20%\pm5%$ $+24%\pm15%$ $+19%\pm10%$</td>
</tr>
<tr>
<td>$(3,5),(4,6)$, b$(1,1), b'(16,7)$</td>
<td>100.9</td>
<td>$+7%\pm10%$ $+2%\pm15%$ $+30%\pm10%$</td>
</tr>
</tbody>
</table>
re-distribution of the \( N_2 \) molecules within the ground state vibrational levels would likely cause a reduction in the excitation of \( c_1^* (\nu=0 \text{ and } 1) \) together with increased excitation of the higher vibrational levels as was observed. A more detailed analysis given below allows us to quantify the observation further.

McConkey <104> showed that the intensity of a vibrational band can be written as:

\[
I_{\nu,\nu'} \propto \frac{i N_{\nu} q_{\nu,\nu'} q_{\nu',\nu}}{\lambda^3} \quad (7-1)
\]

where \( N_{\nu} \) is the number density of lower state molecules which are being excited. \( q_{\nu,\nu'} \) and \( q_{\nu',\nu} \) are the Franck-Condon factors for the upward and downward transitions respectively, and \( \lambda \) is the wavelength of the \((\nu',\nu')\) transition. \( i \) is the electron beam current. If we consider a single downward transition, the \((0,0)\) band for example, then \( \lambda \) and \( q_{\nu',\nu} \) stay constant. The current \( i \) is also kept constant. Therefore, we have from Equation (7-1):

\[
I \propto N_{\nu} q_{\nu,\nu'} \quad (7-2)
\]

For the discharge off, all the population is in \( \nu = 0 \), then

\[
I_{\text{off}} \propto N_0 q_0 \quad (7-3)
\]

For the discharge on, we have populations in all the levels, such as
$n_0, n_1, n_2, n_3, \ldots \text{ in } \nu=0, 1, 2, 3, \ldots$, and hence

$$I_{\text{on}} \propto n_0 q_0 + n_1 q_1 + n_2 q_2 + \ldots \quad (7-4)$$

with

$$N_0 = n_0 + n_1 + n_2 + n_3, \ldots \quad (7-5)$$

Thus the intensity ratio of the (0,0) band with discharge on and off is given by the following:

$$\frac{I_{\text{on}}}{I_{\text{off}}} = \frac{n_0}{N_0} + \frac{n_1}{N_0}q_0 + \frac{n_2}{N_0}q_0 + \frac{n_3}{N_0}q_0 + \ldots \quad (7-6)$$

Using the relative F-C factors measured by Ajello et al. <101>, we have

$$\frac{I_{\text{on}}}{I_{\text{off}}} = \frac{n_0}{N_0} + \frac{n_1}{N_0} \times 0.165 + \frac{n_2}{N_0} \times 0.0162 + \frac{n_3}{N_0} \times 0.0036 + \ldots \quad (7-7)$$

Here, we see immediately because of the fast fall off in the F-C factors with increase in $\nu$ that

$$\frac{I_{\text{on}}}{I_{\text{off}}} = \frac{n_0}{N_0} \quad (7-8)$$

From the present measurement for the intensity change of the (0,0), (0,1) band emissions with a pure $N_2$ discharge, we have an average value $I_{\text{on}}/I_{\text{off}} = 0.84$ which gives the upper and lower limits for the number density ratio $0.8 \leq n_0/N_0 \leq 0.84$ according to Equation (7-7). Take relative values $n_0:n_1:n_2 = 80:15:5$, then Equation (7-7) gives

-114-
\[ \frac{I_{\text{en}}}{I_{\text{eff}}} = 0.8 + 0.025 + 0.001 \approx 0.83 \quad (7-9) \]

This number is very close to the present measurement, 0.84, for the (0,0) and (0,1) band emissions.

To obtain a higher concentration of metastable species, and a higher dissociation fraction of the parent molecules from a discharge source, a gas mixture is often used instead of pure nitrogen. It was found that a He + N\textsubscript{2} mixture increased the concentration of metastable species dramatically \textless 85,103\textgreater. Dissociation of N\textsubscript{2} molecules was greatly improved when Ar atoms were introduced into the N\textsubscript{2} discharge \textless 102\textgreater. It is believed that the energy transfer from excited and ionized He or Ar atoms to the nitrogen molecules caused higher production of metastable species and higher dissociation of nitrogen molecules \textless 85\textgreater. To explore this effect further, we have used gas mixtures of He + N\textsubscript{2} and SF\textsubscript{6} + N\textsubscript{2}. The results are listed in Table 7-1.

Using similar arguments to before, Equation (7-7) leads us to the conclusion that 0.55 \leq n_{\text{0}}/N_{\text{0}} \leq 0.63 for the N\textsubscript{2} + He discharge, and 0.67 \leq n_{\text{0}}/N_{\text{0}} \leq 0.74 for the N\textsubscript{2} + SF\textsubscript{6} discharge. However, since strong FI emissions at 95.5 nm, and 97.5 nm contributed significantly to the signals for the (0,0) and (0,1) bands, the errors involved in the evaluation for the N\textsubscript{2} ground state molecules are large and hard to estimate (20% error is very likely) in the case of the SF\textsubscript{6} + N\textsubscript{2} discharge. The situation is better for the He + N\textsubscript{2} discharge (see Table 7-1).
The strongest $c^1\Sigma_u^+-X^1\Sigma_g^+$ bands (0,0) and (0,1) show the largest negative effects, approximately 36% for the discharge of 85% He + $N_2$. However, a reduction in intensity of about 16% is obtained for the two bands when pure $N_2$ discharge is used. The intensity changes for the (0,0) and (0,1) bands should be the same (neglecting any trapping of resonance radiation), because they come from the same upper level. Any differences shown in Table 7-1 for the cases of He + $N_2$ and SF$_6$ + $N_2$ mixtures are not statistically significant and are due to the difficulty of isolating the individual emissions from FI and other $N_2$ features. As discussed earlier, the $N_2$+SF$_6$ discharge showed unequally-enhanced FI emissions at 95.5 nm and 97.5 nm which are overlapped with the (0,0) and (0,1) bands respectively. This is due to the dissociation of SF$_6$ by the discharge. In spite of this, the (0,0) and (0,1) bands still show a large negative effect of approximately 26%. It is clear that SF$_6$ molecules appear to play an important role in the discharge process.

The energy dependence of the intensity change for the (0,0) band with discharge on and off over the energy range 5 eV to 25 eV is shown in Figure 7-4. The difference reflects the reduction in $X(v=0)$ population when the discharge is switched on as discussed earlier. It is noted that the ratio of the two curves in Figure 7-4 is approximately 0.7. This is quite close to the values deduced in the earlier analysis.

In summary, we have found that the $N_2$+SF$_6$ mixture shows the largest impact on the intensity pattern of the $c^1\Sigma_u^+-X^1\Sigma_g^+$ system when the discharge is turned on. A large amount of He in the $N_2$ discharge also
FIGURE 7-4: Excitation function of $c_1 (0,0)$ with discharge on and off.
shows an enhanced effect over pure $N_2$. No direct evidence of the electronically excited metastable states being excited to the $c'$ states has been found in this work.

7.3.2 The Lyman-Birge-Hopfield (LBH) Band System

LBH band system is a prominent and important UV emission source in the terrestrial dayglow and aurora. Extensive laboratory investigations have been carried out to obtain our current knowledge of this system. Measurements have included electron energy loss experiments <94-95>, direct detection using time-of-flight techniques <96>, and absolute emission measurements <98,99,49>. Chung and Lin calculated the LBH excitation cross sections by electron impact <97>.

As pointed out by Stone and Zipf <82>, a discharge-processed $N_2$ gas beam contains a large number of vibrationally excited $N_2^*$ molecules which alter the emission pattern of the LBH system. We have examined this effect further in the present work. Figure 7-2 shows the partial potential energy curves given by Lofthus and Krupenie <100> for $N_2$ within the 12-15 eV energy region of the Rydberg and valence states. Figure 7-5 shows the spectrum of LBH bands at 100 eV electron impact. Electron beam current was 65 μA. Inlet gas pressure was 55 mTorr closely monitored by a MKS baratron. A large $N_2$ reservoir provided a steady gas flow through the collision chamber for a few days without changing the gas pressure significantly. This allowed the LBH band spectrum with discharge on and off to be obtained under identical conditions (i.e. same gas pressure, same electron beam current, same
FIGURE 7-5: LBH band spectrum of $N_2$ at 100 eV impact energy.
electron energy, and same beam focusing setup.). Then, the individual spectral features were identified, and their emission intensities were measured for the two excitation schemes. The quantitative evaluation of intensity change for each band is given in Table 7-2. For some emission features, there is overlap between nearby lines. In this case, only the dominant band is shown in the spectrum of Figure 7-5 and in Table 7-2.

Although many of the features are quite faint and hence the statistical significance of the data is low in many cases (see Table 7-1 and 7-2), it appears that when the discharge is turned on, a significant population of $N_2$ molecules has been transferred to other vibrational levels of the ground $X^1 \Sigma^+_g$ state from $\nu=0$.

Generally, there are changes in the intensity relations between the bands relating to the progressions with different values of vibrational quantum number $\nu'$ for the upper states. The positive effects for those transitions from higher levels $\nu' = 4, 5$ and 6 reflect the presence of highly vibrationally excited $N_2$ molecules in the target gas as discussed below. For the progressions from $\nu' = 1, 2, 3$, the effects are all negative ranging from $-2\%$ to $-20\%$, while the effects are all positive for the progressions from $\nu' = 4, 5, 6$ with the largest changes $+36\%$ for the (6,4) band, and $+20\%$ for the (5,1) band. The only exception in the positive effect for the $\nu' = 6$ progression is a slight negative effect for the (6,3) band ($-2\%$). The probable explanation for this is that the (6,3) band is overlapped by the (3,1) band which is expected to experience a negative effect (see Table 7-2).
<table>
<thead>
<tr>
<th>Band ($v', v''$)</th>
<th>Wavelength (nm)</th>
<th>Intensity Change for Pure $N_2$ Discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>$NII^3 D^0 - , ^3 P$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(6,0)</td>
<td>127.3</td>
<td>+8%±5%</td>
</tr>
<tr>
<td>$NI^2 P^0 - , ^2 D$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(6,1)</td>
<td>131.2</td>
<td>+7%±5%</td>
</tr>
<tr>
<td>(6,3)/(3,1)</td>
<td>139.6</td>
<td>-2%±10%</td>
</tr>
<tr>
<td>(6,4)</td>
<td>144.1</td>
<td>+36±20%</td>
</tr>
<tr>
<td>(5,0)</td>
<td>129.9</td>
<td>+4%±5%</td>
</tr>
<tr>
<td>(5,1)</td>
<td>133.9</td>
<td>+20±10%</td>
</tr>
<tr>
<td>(5,3)</td>
<td>142.7</td>
<td>+4%±10%</td>
</tr>
<tr>
<td>(5,4)</td>
<td>147.4</td>
<td>+6%±15%</td>
</tr>
<tr>
<td>(4,1)</td>
<td>136.8</td>
<td>+9%±10%</td>
</tr>
<tr>
<td>$N^2 P^0 - , ^2 P$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4,2)</td>
<td>141.2</td>
<td>+3%±5%</td>
</tr>
<tr>
<td>(4,3)</td>
<td>145.9</td>
<td>+6%±15%</td>
</tr>
<tr>
<td>(3,0)</td>
<td>135.4</td>
<td>-20%±10%</td>
</tr>
<tr>
<td>(3,1)/(6,3)</td>
<td>139.8</td>
<td>-2%±10%</td>
</tr>
<tr>
<td>(3,2)</td>
<td>144.4</td>
<td>-13%±10%</td>
</tr>
<tr>
<td>(2,0)/(5,2)</td>
<td>138.4</td>
<td>-20%±10%</td>
</tr>
<tr>
<td>(2,1)</td>
<td>143.0</td>
<td>-7%±10%</td>
</tr>
</tbody>
</table>
From Table 7-2, the average drop in intensities for the (3,0) and (3,2) bands is 16% with the discharge on. Thus \( \frac{I_{on}}{I_{off}} = 0.84 \) for the upper level \( v' = 3 \). Using the relative values \( n_0:n_1:n_2 = 80:15:5 \) as before for the same pure \( N_2 \) discharge and the F-C factors given by Lofthus and Krupepinie \( <100> q_0 = 0.1832, q_1 = 0.0123, q_2 = 0.0758, q_3 = 0.0686 \), we predict that

\[
\frac{I_{on}}{I_{off}} = 0.8 + 0.01 + 0.02 = 0.83
\]

Again, this number is coincident with our measured value of 0.84, and confirms our previous conclusion that \( n_0/N_0 = 0.8 \).

For the upper level of \( v' = 4 \), our measured average intensity change for the (4,1) and (4,3) bands is a slight increase of about 7%, i.e., \( \frac{I_{on}}{I_{off}} = 1.07 \). This means that there must be some transitions with upward F-C factors larger than that for the (0->4) transition. From the F-C factors given by Lofthus and Krupepinie \( <100> \), we find \( q_0 = 0.160, q_{10} = 0.1161, q_{11} = 0.1644, q_{12} = 0.1136 \). Clearly these data coupled with Equation (7-6) make it clear that a measured value of \( \frac{I_{on}}{I_{off}} > 1 \) suggests a significant population in high vibrational states particularly \( v' = 11 \). For the case of \( v' = 5 \), the F-C factors \( <100> \) are such \( (q_0 = 0.1217, q_{12} = 0.1472, q_{13} = 0.1481) \) that the increase in the intensity of the \( v' \) progression measured in this work implies significant populations in \( v' = 12 \) and/or \( v' = 13 \) of the ground state.

Significant populations of these high-lying levels, when the discharge is on, is not unreasonable, due to the fact that copious quantities of \( N_2^+ \)
can be created within the discharge. There is a huge $N_2$ resonance peaked around 2.5 eV ($\nu = 9$) and the $N_2$ and $N_2^-$ energy curves overlap in just this energy region $\langle 100 \rangle$. Hence decay of the $N_2^-$ would be into these high vibrational levels of the ground state. Our relative intensity measurements are not of sufficient statistical accuracy to enable us to draw definite conclusions regarding actual populations, but our results are consistent with approximately 80% of the molecules in the $\nu=0$ ground state, and the rest in excited levels, most likely with $\geq11$.

Selective excitation of a particular vibrational level of $N_2$ molecules by a R.F. discharge source is impossible. Certainly, it is beyond the capacity of current techniques to produce a molecular beam all in a definite vibrational state other than the ground state. The present work, although it doesn't seem to have the sensitivity to predict the detailed population for each vibrational level, does seem to be able to make reasonable predictions about the population in the $\nu=0$ level. More careful measurements (to the 1% level) would be required to enable us to extract accurate populations of the other levels using the analysis discussed above.

7.3.3 NI and NII Emissions

A positive enhancement was found for all the NI and NII emissions studied when the discharge source was used. Table 7-5 gives the results for all NI and NII emissions enhanced by the discharge effect at 200 eV electron impact. The $N_2 + SF_6$ mixture shows the largest enhancement for the NI and NII emissions which must be due to greater
<table>
<thead>
<tr>
<th>Species Term</th>
<th>Wavelength (nm)</th>
<th>Intensity Change for Various Discharge</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NII } g^3P \to g^3P )</td>
<td>91.7</td>
<td>( +6% \pm 5% )</td>
<td>( +1% \pm 10% )</td>
</tr>
<tr>
<td>( \text{NII } g^3P \to D^0 )</td>
<td>108.5</td>
<td>( +6% \pm 5% )</td>
<td>( +5% \pm 5% )</td>
</tr>
<tr>
<td>( \text{NI } g^4S \to g^4P )</td>
<td>113.4</td>
<td>( +5% \pm 10% )</td>
<td>( +45% \pm 10% )</td>
</tr>
<tr>
<td>( \text{NI}^2 D^0 \to F )</td>
<td>116.8</td>
<td>( +12% \pm 10% )</td>
<td>( +11% \pm 10% )</td>
</tr>
<tr>
<td>( \text{NI}^2 D^0 \to P )</td>
<td>117.7</td>
<td>( +32% \pm 10% )</td>
<td>( +15% \pm 10% )</td>
</tr>
<tr>
<td>( \text{NI } g^4S \to g^4P )</td>
<td>120.0</td>
<td>( +2% \pm 5% )</td>
<td>( +18% \pm 5% )</td>
</tr>
<tr>
<td>( \text{NI}^2 D^0 \to D )</td>
<td>124.3</td>
<td>( +8% \pm 10% )</td>
<td>( +7% \pm 10% )</td>
</tr>
</tbody>
</table>
dissociation of \( N_2 \) molecules in this discharge. It should be noticed that
the emission rate of most NI and NII lines in this spectral region is not
strong (except for the NI 120 nm and NII 108.5 nm features), and thus
the statistical uncertainties are quite high. The normally quite small
positive effects for NI and NII emissions with pure \( N_2 \) discharge gas
reflect a rather small dissociation of nitrogen molecules in the R.F
discharge source.

The energy dependence of the discharge effect on the NI 120 nm
emission is shown in Figure 7-6. A clear energy shift shows up, which
indicates the existence of target species other than molecular nitrogen,
most probably atomic nitrogen. Figure 7-7 gives a close look at the
threshold excitation of NI 120 nm emission with discharge on up to 20 eV
(below the threshold energy for the excitation of NI 120 nm from the
ground state nitrogen molecules). Stone and Zipf’s result <81-82> is also
shown in Figure 7-7 for comparison. They also found evidence for the
presence of vibrationally excited \( N_2 \) molecules in their target beam.

As mentioned earlier, the \( N_2 + SF_6 \) discharges produced the largest
change to all the VUV emissions studied in this work. The reason is not
perfectly understood at this point. \( SF_6 \) molecules have a very large
electron capture cross section <105> and a very large electron affinity
<106>. Also the excited \( SF_6^+ \) formed after electron capture has a very
long autodetachment lifetime, and \( SF_6^+ \) obtained after collisional stabilization is very unreactive <107>. The electron detachment cross sections
FIGURE 7-6: Excitation function of NI 120 nm with discharge on and off. Note the contributions from various species when discharge is on.
FIGURE 7-7: Excitation function of NI 120 nm below 20 eV from various species other than $N_2$ when discharge is on.
for $SF_6^-$, $SF_6^-$ and $F^-$ on $SF_6$ molecules have their onsets at 90 eV, 90 eV and 8 eV respectively <107>. Because the $SF_6$ molecules tend to mop up the low energy end of the electron energy distribution in the discharge, this distribution develops an enhanced high energy contribution which causes, in turn, enhanced dissociation or vibrational excitation of $N_2$ molecules in the discharge.

Assuming Stone and Zipf's <81,82> cross section for the NI 120 nm production from atomic N together with the accepted cross section for its production from $N_2$ <69> allows us to obtain a value for the relative number densities of N and $N_2$ produced by the different discharge gas mixtures. We found that 0.07%, 0.6% and 0.7% of the $N_2$ molecules were dissociated for pure $N_2$, $N_2+85\%He$ and $N_2+10\%SF_6$ discharges respectively. Considering the huge uncertainty in the cross section of Stone and Zipf <82>, our dissociation fractions deduced using their cross section data carry a similar amount of uncertainty, and thus must be regarded as only approximate.

7.4 CONCLUSIONS

VUV emissions following electron impact on R.F. discharge - processed $N_2$ target gas have been studied in the wavelength region 90-150 nm. The intensity change pattern for the LBH system indicated a reduction in population for the low levels $\nu' = 1, 2, 3$, and a population increase for the higher levels $\nu' = 4, 5, 6$. The strongest molecular emissions of $N_2$ in the VUV region; the $c_4^\ast (0,0)$ and (0,1) features are both significantly depressed when the discharge is switched on, particularly
when the discharge mixtures are used. A simple analysis suggests that close to 80% of the $N_2$ molecules are in the $v=0$ state, when pure $N_2$ discharges are used. Many of the remainder are in higher states, around $v=12$. All NI and NII emissions are enhanced at 200 eV electron energy, but the enhancement is most obvious near threshold. This is due to excitation from atomic and possibly metastable molecular species.
CHAPTER VIII: EMISSION CROSS SECTIONS OF THE RESONANCE LINES 
INDUCED BY ELECTRON IMPACT ON ATOMIC OXYGEN

8.1 INTRODUCTION

VUV emissions of atomic oxygen are prominent features in the spectra of the airglow of the Earth and aurora as well as the atmosphere of Venus and Mars <108-109>. On Earth, daytime excitation of atomic oxygen proceeds by impact of electrons in the photoelectron ambient distribution which have energies up to 60 eV <110>. At high latitudes, auroral precipitated electrons as well as direct entry electrons from the solar wind also produce excitation of atomic oxygen. As a result, the optical emissions of atomic oxygen dominate the VUV airglow and auroral emission spectra. The observation from the ground and from satellites of strong OI emissions in the VUV region provides a remote-sensing technique for the studies of the chemistry and dynamics of atomic oxygen in the thermosphere. Unfortunately, the investigation of these interesting problems has been hindered by a lack of accurate cross section data. The differential and integrated electron impact excitation cross sections of atomic oxygen have been measured by Doering et al. <111-117>. The OI 130.3 nm emission cross sections of atomic oxygen induced by electron impact were measured by Stone and Zipf in 1974 <118>. Recently Zipf and Erdiman <83> re-measured these cross sections, and reduced their data by a factor of 2.8 to reflect the change in the normalization standard since their earlier work. However, some questions have been raised regarding the reliability of some of their revised cross sections <114-115>. Since Zipf et al. are the only group who have

-130-
carried out measurements of the VUV emission cross sections of atomic oxygen by electron impact, more experiments are definitely needed to clear the discrepancy which exists presently, and to provide reliable cross sections for the modeling of the OI VUV emission related phenomena.

Other experiments involving electron and atomic oxygen collisions include low energy total electron scattering cross sections <120>, electron impact ionization <121>, emission cross section measurements of OI 777.4 nm (the major cascade contribution to OI 135.6 nm emission) <122>, and lifetime measurements and oscillator strengths for some VUV transitions <123>. Theoretical calculations have been performed actively over the last two decades. Routree and Henry calculated the electron impact excitation cross sections of the atomic oxygen \(2p^3P - 3s^3S^0\) transition using uniterized Born, nonexchange, and close-coupling approximations in 1972 <124>, and later, in 1977, Routree did the calculation again using a close-coupling expansion carefully choosing the oscillator strength <125>. Kazaks et al. calculated the generalized oscillator strengths and total cross sections for electron impact excitation and ionization <126>. Sawada and Ganus calculated the scattered electron angular distributions and integrated cross sections using distorted-wave potentials <127>. Smith performed calculations of electron impact excitation cross sections using a close-coupling formalism including exchange <128>. Cascade and radiation trapping effects for atomic oxygen emissions following electron impact were calculated by Julienne and Davis using a distorted wave method in 1976 <129>. While more recently, Tayal and Henry calculated oscillator strengths and electron impact excitation cross sections
Very recently, these authors calculated differential cross sections, and compared their calculations with available experimental data. It should be mentioned that the theoretical calculations are not consistent with each other in either magnitude or shape of the excitation functions. In addition, experimental data are mainly from two groups, electron scattering measurements by Doering et al. and emission cross section measurements by Zipf et al. In the case of cascade-free emissions, the integrated electron scattering cross sections are equal to the emissor cross sections provided branching ratios are properly allowed for. This means that the results from these two groups can only be compared with confidence when cascade contributions are small, or when they can be allowed for adequately.

Present work was designed to measure absolute VUV emission cross sections following electron impact as a function of impact energy. To make this work independent and unique from previous experiments, a different technique for producing atomic oxygen and measuring its number density has been used. Previously (83,111,118), molecular oxygen was used as the parent molecule to provide atomic oxygen via dissociation in a microwave discharge. The vibrationally excited oxygen molecules produced by the discharge are metastable and do not decay to the v=0 ground state because of the zero dipole moment of oxygen molecules. Their contributions to dissociative excitation have been assumed to be identical to those from ground state molecules. It is not clear that this assumption is justified. In this work, nitric oxide (NO) is used to produce atomic oxygen via a R.F. discharge source. Any excited nitric oxide molecules relax immediately to the v=0 state by vibrational
transitions within the ground state. This eliminates the presence of metastable species in the target gas. Molecular emissions from NO ions in the VUV region are used to determine the dissociation fraction of the target gas. Since the O atom density is obtained directly, a further measurement of this parameter becomes unnecessary, and reduces the largest source of error usually involved in this type of cross section measurement.

3.2 EXPERIMENTAL TECHNIQUES

3.2.1 Dissociation of NO Molecules by the R.F. Discharge

The R.F. discharge source used in this work has been described in Chapter IV and Chapter VII. This R.F. discharge source worked extremely well for the dissociation of hydrogen molecules <42>, and again was used to dissociate NO molecules in this work. The potential energy curves given by Gilmore <132> for NO and NO⁺, and by Albritton et al. <133> for NO⁺ show that the dissociation of ground state NO molecules by electron impact via the lowest repulsive state NO ²Σ⁺ needs an onset energy about 8.7 eV, even though the dissociation limit of NO molecules is 6.5 eV at large internuclear distance. Figure 8-1 gives a partial potential energy diagram for the NO molecule and NO⁺ ion. The results for NO dissociation are very good, and are given in Table 8-1 for various NO gas pressures in the discharge tube. A dissociation of 70% of the NO molecules was obtained under the optimum discharge conditions. The following method for determining these dissociation fractions was used.
8.2.2 Dissociation Fraction of NO Molecules

It should be mentioned that the N atoms produced in the discharge react strongly with NO molecules to yield more O atoms via the reaction $N + NO \rightarrow O + N_2$. This effect is seen by the presence of some $N_2$ emissions (see Figure 8-9). We note that since this reaction results in one O atom for each NO molecule lost, it does not affect the discussion in this section.

The determination of the atomic oxygen number density in a mixed target gas is absolutely critical to the absolute cross section measurement. However, it is extremely difficult in a crossed-beam experiment to obtain an accurate value for the effective number density of a certain species in a mixed beam because of the difficulty of establishing the beam overlap factor in the electron–target interaction region. Systematic errors in the determination of atomic oxygen number densities by optical absorption techniques have led to reported errors as high as 200% in the absolute cross section measurements <83>. Various techniques have been used to get around this serious problem. Most of these involve the use of some reference species as a comparison standard. For example, Doering and Vaughan <111> used He or H as the comparison standards making use of the fact that in an electron energy-loss experiment the relative signals from the different species in the target are related to the cross section (or the oscillator strength)
FIGURE 8-1: Partial energy curves for NO and NO⁺.
ratio and to the number density ratio of the two features being compared. Thus, the number density of the atomic oxygen is expressed in terms of a few known factors. A similar technique was used by Zipf (134) who compared the ionization cross section ratio of electron impact on atomic and molecular oxygen to obtain the number density ratio of these two species in the target gas. Obviously, the accuracy of this type of technique depends heavily on the accuracy of the data used (oscillator strength, ionization cross section, etc.).

A different technique has been developed in this laboratory for the determination of the dissociation fraction produced by the R.F. discharge. It should be mentioned that this technique can only be applied to certain diatomic molecules. The products of a discharge through a diatomic molecular gas, AB, can only be (1) A atoms, (2) B atoms, (3) undissociated AB molecules (4) A⁺, B⁺, AB⁺, A⁻, B⁻, AB⁻ ions, (5) A⁺, B⁺, AB⁺ excited metastable species, (6) A⁺⁺, B⁺⁺, AB⁺⁺ excited metastable ions. Clearly we want to get rid of unwanted species in the target gas beam. But some parent, AB, molecules are unavoidable, and will always be present in the target gas beam. The key to the present technique is to eliminate the dissociation products (4), (5), and (6). To do this, a specially shaped nozzle was used at the outlet of the discharge source (see Figures 4-1, 4-2), which forced all the particles leaving the discharge to make several collisions with the wall of the discharge tube in addition to any collisions with other discharge products. A thermalized gas beam was produced as a result of these multi-collisions; any ions had ample time to combine and excited species were removed by radiative decay or collisional quenching. This
discharge source was found to eliminate all the ions and excited species in the \( H_2 \) discharge experiment <19>. However, for some metastable species, vibrationally excited \( N_2 \) molecules for example, collisional and wall quenching are less effective, and some metastable species were found to remain in the target gas beam as discussed in Chapter VII.

As a monitor of the number density of undissociated NO molecules in the target beam, we used the \( A~^1\Pi - X~^1\Sigma \) bands of \( NO^- \) (see Figure 8-1). This intensity produced by electron impact, is directly proportional to the NO number density in the target. The discharge reduces the concentration of NO molecules in the gas beam by dissociating a fraction of these, and thus reduces the emission rate of the \( NO^+ \) bands. It is the change in the NO concentration in the target that controls such an emission rate when the discharge is turned on and off, since the products from the discharge are well thermalized and thus the NO velocity does not change. If the discharge-on/off signals are expressed as \( S_{on}(NO^-) \) and \( S_{off}(NO^-) \), then by Equation (4-9), Chapter IV, the dissociation fraction of NO molecules is given by:

\[
D = 1 - \frac{S_{on}(NO^-)}{S_{off}(NO^-)}
\]  

(8-1)

The intensities of the \( NO^+(A^1\Pi \rightarrow X^1\Sigma^-) \) bands (1,0) at 134.0 nm, (1,1) at 138.3 nm, and (0,2) at 146.1 nm have been used in the determination of the dissociation fraction of NO molecules in the discharge. Identical results have been obtained using these independent features, thus establishing the reliability of the technique described above. Table 8-1
gives the various dissociation fractions obtained under different NO pressures. At least 25% He atoms were added to the NO discharge for all the measurements discussed in this chapter.

8.2.3 Cross Section Expression

The rate of an emission induced by electron impact on atomic target is given by Equation (4-19) in Chapter IV:

\[ S(O) = S_{on}(O) - (1-D)S_{off}(O) \]  \hspace{1cm} (8-2)

where \( S_{on} \) and \( S_{off} \) are the signals for the same emission feature with the discharge on and off respectively. Taking into account line polarization and other factors, we get an expression for the emission cross section of a particular spectral line from electron impact on atomic oxygen as:

\[ \sigma = \frac{S(1-p/3)}{Kf(P)I\eta\Lambda(P)\xi} \]

by Equation (8-2)

\[ \frac{(S_{on}-(1-D)S_{off})(1-p/3)}{Kf(P)I\eta\Lambda(P)\xi} \]  \hspace{1cm} (8-3)

where \( p \) is the polarization of the emitted feature; \( K \) is a geometrical factor; \( I \) is the electron current; \( \eta \) is the sensitivity of the detector; \( \xi \) is the instrumental polarization sensitivity of the system; \( f(P) \) is the pressure function given by Equation (2-61); and \( \Lambda(P) \) is the trapping factor given by Equation (4-13). Resonance trapping for atomic oxygen emissions in the VUV region is very serious because of the large
TABLE 8-1
Dissociation Fractions of NO molecules Determined by Simultaneous Ionization - Excitation of NO Molecules

<table>
<thead>
<tr>
<th>NO Pressure (mTorr)</th>
<th>He added (%)</th>
<th>Dissociation Fraction Determined by $\text{NO}^\ast(A^1\Pi - X^1\Sigma^\ast)$ Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(c,2) 146.1 nm</td>
<td>(1,0) 134.0 nm</td>
</tr>
<tr>
<td>5-6</td>
<td>90%</td>
<td>24%</td>
</tr>
<tr>
<td>11-12</td>
<td>80%</td>
<td>40%</td>
</tr>
<tr>
<td>22-23</td>
<td>50%</td>
<td>54%</td>
</tr>
<tr>
<td>32-33</td>
<td>50%</td>
<td>63%</td>
</tr>
<tr>
<td>42-44</td>
<td>30%</td>
<td>75%</td>
</tr>
<tr>
<td>52-55</td>
<td>25%</td>
<td>66%</td>
</tr>
</tbody>
</table>
oscillator strengths for some of the OI resonance lines. This will be discussed in the next section. The determination of the absolute emission cross section is based on a comparison between a feature to be measured and a feature with known cross section, which in our case is the Lyman α line from dissociative excitation of molecular hydrogen by 200 eV electron impact. The polarization of \( H_2 \) Lyman α at 200 eV energy is less than 4%, thus, the correcting factor \( (1-p/3) \) is slightly over 1% which can be dropped without causing much error. The polarization of atomic oxygen lines is not known, however at energies greater than 100 eV, it is expected to be no more than a few percent, and its correcting factor is negligible compared to the error involved with the standard cross section (9% for \( H_2 \) Lyman α at 200 eV). Since we are basically dealing with essentially unpolarized radiation, the instrumental polarization sensitivity cancels out when a comparison between two cross sections is made. The electron current is kept constant for the comparison, and thus cancels out too. The trapping factor for \( H_2 \) Lyman α is unity because of the low number density of H atoms in the collision region. Hence according to Equation (8-3), the ratio of two cross sections becomes:

\[
\frac{\sigma_u}{\sigma_r} = \frac{[S_{\alpha \alpha} - (1-D)S_{\alpha f}]}{S_r f(P_u) \eta_u A_u(P_u)} f(P_r) \eta_r \frac{\eta_u A_u(P_u)}{P_u}
\] (8-4)

or

\[
\frac{\sigma_u}{\sigma_r} = \frac{[S_{\alpha \alpha} - (1-D)S_{\alpha f}]}{S_r f(P_u) \eta_u A_u(P_u)} \frac{\eta_r}{P_r}
\] (8-5)

where \( r \) refers to the reference line, \( H_2 \) Lyman α in this case, and \( u \) represents the unknown line which is one of the atomic oxygen lines.
measured in this work. This equation was the basic formula used in this work for the absolute emission cross section evaluations. Each comparison was made over a short time interval to minimize the possible fluctuations in the system. Many comparisons were made independently, the average was taken as the final result presented in this thesis.

8.2.4 Trapping Effect of Resonance Radiations

Trapping of resonance lines is expected to be the major problem in determining the absolute cross sections for the OI resonance lines at 130.3 nm, 102.7 nm, 98.9 nm, and 87.8 nm because of large fraction of atomic oxygen in the target beam. Since the oscillator strengths of these lines are quite different, the trapping effect varies accordingly. The observed signal for a resonance emission is reduced by a trapping factor $A(P)$ which is given by Equation (4-13) as:

$$A(P) = \exp[-\epsilon f(P)]$$  \hspace{1cm} (8-6)

where

$$\epsilon = c \beta G(L) f \lambda \sqrt{M/T}$$  \hspace{1cm} (8-7)

where $c$, $\beta$, and $G(L)$ are geometrical factors of the system. $f(P)$ is the pressure function given by Equation (2-61). $M$ is the mass of the target atom, oxygen in this case. $T$ is the temperature. $\lambda$ and $f$ are the wavelength and the associated oscillator strength. The geometrical factors were obtained by computer fitting of the OI 130.3 nm emission intensity versus atomic oxygen density. Then, the trapping effects for other resonance lines were calculated using the known oscillator strengths for the transitions involved. Figure 8-2 shows the curve for
the OI 130.3 nm intensity versus atomic oxygen pressure. The trapping effect is clearly seen. The calculated trapping effects for other OI resonance lines are given in the corresponding text, and the oscillator strengths for atomic oxygen are listed in Table 8-2. Both experimental and theoretical results are listed from several independent measurements and calculations, and the values recently measured by Doering et al <136> were used for calculations of the trapping effect. Their results have been highly recommended in the recent review articles about atomic oxygen <137,138>. The huge difference exists for the OI 98.9 nm line for which the emission cross section of Zipf and Erdman <83> is 2-3 times larger than the excitation cross section of Vaughan and Doering <113,115> even at 20 eV energy where the cascade contribution should not be so significant, especially when some of the upper states cascading to the 3s'7D0 state also have a probability of autoionizing <115>. Differences are also present in the case of the OI 102.7 nm, and the OI 87.8 nm lines <114>. It is noted that no discussion regarding trapping effect of resonance lines was made in the optical measurements of Zipf et al. <83,134>. This thesis will suggest that some of the inconsistencies between the optical measurements by Zipf et al. and the electron energy-loss measurements by Doering et al. are due to trapping effects of resonance lines.

8.2.5 Error Analysis
FIGURE 8-2: The variation of the OI 130.3 nm emission rate with atomic oxygen partial pressure.
### Oscillator Strengths for Atomic Oxygen Resonance Transitions

<table>
<thead>
<tr>
<th>State</th>
<th>Wavelength (nm)</th>
<th>Experimental Results</th>
<th>Theoretical Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>OI $3s^3P^0$</td>
<td>87.8</td>
<td>0.086</td>
<td>0.079</td>
</tr>
<tr>
<td>OI $3s^3D^0$</td>
<td>98.9</td>
<td>0.061</td>
<td>0.058</td>
</tr>
<tr>
<td>OI $3d^3D^0$</td>
<td>102.7</td>
<td>0.019</td>
<td>0.020</td>
</tr>
<tr>
<td>OI $3s^3S^0$</td>
<td>130.3</td>
<td>0.048</td>
<td>0.048</td>
</tr>
<tr>
<td>OII $2p^4P$</td>
<td>83.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*These values are used for the calculations of resonance trapping effect for OI 98.9 nm, OI 102.7 nm, and OI 87.8 nm features.*
The errors involved in the evaluation of the absolute emission cross sections are normally from 4 principal sources: (1) the uncertainty in the relative calibration of the optical system, 10% in the wavelength range 90-120 nm, and 20% in 80-90 nm; (2) uncertainty in the normalization standard, 9% in this case for Lyman α from \( H_2 \) at 200 eV; (3) statistical errors involved in the emission rate, including 2% statistical fluctuation for the counting system, 2% in the fluctuation of electron current, 2% in the gas pressure variation, and 10% in the determination of dissociation fraction; (4) uncertainty in the trapping coefficient for the OI 130.3 nm feature obtained by computer fitting of the curve given in Figure 8-2, 50% given by statistical F-test.

The measurement on the excitation function is often affected by variations in the interaction volume with change in electron energy, or the varying electron path length in the magnetic field. This has been checked by measuring the known excitation function for the ArI 104.8 nm line \(<135>\). Figure 8-3 shows the performance of our electron gun for ArI 104.8 nm which is corrected for the variation of electron current with energy shown in Figure 8-4. Electron current shows some deviations over 0-100 eV range (see Figure 8-4). This has been corrected in all the measurements discussed later.

3 RESULTS AND DISCUSSIONS

8.3.1 The \( 2p \ ^3P \rightarrow 3s \ ^3S^0 \) Transition at 130.3 nm

The energy level diagram of atomic oxygen is given in Figure 8-5
FIGURE 8-4: Electron current variation with energy for our electron gun.
FIGURE 8-5: Partial energy level diagram of atomic oxygen.
which clearly shows all the resonance transitions in the VUV region. The \(2p \ 3P - 3s \ 3S^0\) excitation of atomic oxygen by electron impact is by far the most widely investigated of all atomic oxygen transitions. However, the reactive nature of atomic oxygen makes the measurements very difficult. This results in plenty of theoretical calculations but little experimental data. Stone and Zipf \(<118>\) measured the emission cross sections for the OI 130.3 nm multiplet by electron impact on atomic oxygen (1974). Zipf and Erdman \(<83>\) subsequently revised these cross sections and lowered the absolute values by a factor of 2.8 (1985). Recently, Doering and Vaughan \(<111>\), and Vaughan and Doering \(<112>\) measured the cross section for direct electron impact excitation of atomic oxygen to the \(3s \ 3S^0\) state in the electron energy-loss experiment over the energy range up to 200 eV (1986). More recently, Gulcicek and Doering \(<115>\) redesigned their apparatus with an emphasis on the low energy performance of the electron gun, and measured the direct excitation cross sections for the \(2p \ 3P - 3s \ 3S^0\) transition at low energies (1988). Their new results for this transition agreed with their earlier measurements for electron energies above 30 eV, but doubled their cross section values at 16.5 eV and 20 eV. This resulted in a huge change in the energy dependence of this excitation process at low energies \(<115>\).

Theoretical calculations for the electron impact excitation cross sections of atomic oxygen to the \(3s \ 3S^0\) state have been carried out extensively over the last two decades. The results show much scatter in both the general shape of the energy dependence of the cross section and its absolute value. The theoretical cross sections of Smith \(<128>\) (1976), and
Tayal and Henry (1988) show reasonable overall agreement with the experimental results (83,112,113,116). The calculations of Smith (128) fit the experimental results of Doering et al. (112,113) for the entire energies from threshold to 200 eV, but are a factor of 2 lower than the revised values of the same group (115) at energies below 30 eV. Tayal and Henry's calculations (130) agree with the revised cross sections of Gulcicek and Doering (115) at energies below 30 eV, but are a factor of 1.3 larger at energies above 30 eV. The calculations of Julienne and Davis (129) (1976), and Rountree and Henry (124) (1972) if scaled upward by factors of 1.6 and 1.3 respectively, also match the recent experiments.

The well established cross sections of Lyman α from H₂ at 200 eV and 100 eV (42) have been used as the normalization standard. The linearity of the signal for HI 121.6 nm radiation versus H₂ pressure is clearly demonstrated in Figure 8-6. Trapping effect for the OI 130.3 nm has been measured (see Figure 8-2). This was later used for the evaluation of the absolute emission rate for the OI 130.3 nm feature. Identical conditions were established for the comparison between the two features, including the same gas pressure (H₂ for Lyman α emission and NO for the OI 130.3 nm), the same electron beam current at 150 µA, and the same electron beam focusing setup. Over twenty comparisons have been made between these two transitions over a period of over three months from Feb 91 to April 91, Table 8-3 lists these results. The average value of the emission cross section for the OI 130.3 nm multiplet at 100 eV has been established to be 7.7 x 10⁻¹⁸ cm². This value is 20% lower than the emission cross section of Zipf and Erdman (83), and 20% higher.
FIGURE 8–6: The variation of the HI 121.6 nm emission rate with $H_2$ pressure.
TABLE 8-3

22 Separate Determinations of the OI 130.3 nm Emission Cross Section Following 100 eV Electron Impact on Atomic Oxygen

<table>
<thead>
<tr>
<th>Determination Date</th>
<th>NO Pressure (mTorr)</th>
<th>Dissociation Fraction</th>
<th>Emission Cross Section (10^{-18} cm^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Feb 4</td>
<td>64</td>
<td>83%</td>
<td>8.2</td>
</tr>
<tr>
<td>2. Feb 12</td>
<td>46</td>
<td>74%</td>
<td>6.4</td>
</tr>
<tr>
<td>3. Mar 4</td>
<td>18</td>
<td>69%</td>
<td>7.2</td>
</tr>
<tr>
<td>4. Mar 5</td>
<td>37</td>
<td>74%</td>
<td>7.5</td>
</tr>
<tr>
<td>5. Mar 19</td>
<td>11</td>
<td>37%</td>
<td>7.6</td>
</tr>
<tr>
<td>6. Mar 20</td>
<td>6</td>
<td>21%</td>
<td>7.1</td>
</tr>
<tr>
<td>7. Mar 26</td>
<td>42</td>
<td>71%</td>
<td>9.0</td>
</tr>
<tr>
<td>8. Mar 27</td>
<td>45</td>
<td>60%</td>
<td>8.6</td>
</tr>
<tr>
<td>9. Mar 28</td>
<td>23</td>
<td>54%</td>
<td>9.0</td>
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<tr>
<td>10. Mar 29</td>
<td>22</td>
<td>53%</td>
<td>8.2</td>
</tr>
<tr>
<td>11. Apr 1</td>
<td>22</td>
<td>53%</td>
<td>7.1</td>
</tr>
<tr>
<td>12. Apr 1</td>
<td>42</td>
<td>71%</td>
<td>7.4</td>
</tr>
<tr>
<td>13. Apr 2</td>
<td>33</td>
<td>68%</td>
<td>7.7</td>
</tr>
<tr>
<td>14. Apr 3</td>
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<td>63%</td>
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<td>15. Apr 4</td>
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<td>17. Apr 8</td>
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<td>18. Apr 9</td>
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<td>19. Apr 9</td>
<td>33</td>
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<td>7.3</td>
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<td>20. Apr 9</td>
<td>13</td>
<td>33%</td>
<td>6.8</td>
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<td>21. Apr 10</td>
<td>7</td>
<td>22%</td>
<td>8.8</td>
</tr>
<tr>
<td>22. Apr 10</td>
<td>61</td>
<td>70%</td>
<td>7.4</td>
</tr>
</tbody>
</table>

AVERAGE: 7.7
than the cascade-free excitation cross section of Doering et al. 
<111,112,113,115> at this energy. Considering the errors involved in 
these measurements, this level of agreement is quite satisfactory.

Figure 8-7 shows our measured energy dependence of the OI 130.3 nm 
feature up to 100 eV. Table 8-4 gives the emission cross sections of the 
OI 130.3 nm multiplet at various energies up to 100 eV. For comparison, 
the measured emission cross sections of Zipf and Erdman <83>, and the 
measured cascade-free direct excitation cross sections of Doering et al. 
<113,115>, are also listed in the table. Because of the differences, 
discussed previously, between the various theoretical and experimental 
data for this state, it is very important to demonstrate that the 
measured shape is not influenced by any of the experimental parameters. 
One possible factor which could perturb the shape of the measured 
excitation function is the polarization of the emitted radiation (Equation 
8-3). Fortunately, in the case of the OI 130.3 nm line, the upper state 
involved (3s \(^3S^0\)) is spherically symmetric, and thus the radiation is 
unpolarized. Possible effects due to variations in the interaction volume 
with change in electron energy or to varying electron path length in 
the magnetic field have been checked by making measurements of known 
excitation functions, for example, ArI 104.8 nm as discussed earlier.

Figure 8-8 shows the comparison of our measured excitation function of 
the OI 130.3 nm emission with the similar measurements of Zipf and 
Erdman <83>, the cascade-free excitation cross sections of Doering et al. 
<112,113,115>, and the theoretical excitation cross sections of Smith <128>
FIGURE 8-7: Our measured excitation function of OI 130.3 nm.
<table>
<thead>
<tr>
<th>Electron Energy (eV)</th>
<th>Emission Cross Section Present Result</th>
<th>Emission Cross Section Zipf &lt;83&gt;</th>
<th>Excitation Cross Section Doering et al. &lt;113,115&gt;</th>
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<td>12.5</td>
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<td>13.87</td>
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<td>9.82±30%</td>
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<td>16.5</td>
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<td></td>
<td>10.53±30%</td>
</tr>
<tr>
<td>20</td>
<td>10.7</td>
<td>16.9</td>
<td>11.12±30%</td>
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<td>30</td>
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<td>8.69±30%</td>
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<td>85</td>
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<tr>
<td>100</td>
<td>7.7</td>
<td>9.48</td>
<td>6.30±1.0</td>
</tr>
</tbody>
</table>

The unit for the cross section data is $10^{-18}$ cm$^2$. The error involved in the present data is 25%.
FIGURE 8-8: Excitation function of the OI 130.3 nm multiplet by electron impact on atomic oxygen.
and Tayal and Henry <130>. The theoretical excitation functions are in overall agreement with the present measurement. However, since these calculations do not include any cascade contributions to the excitation of the 3s $^3S^0$ state, their cascade-free cross sections should be smaller than the emission cross sections by an appropriate amount. The measured cascade-free excitation cross sections of Doering et al. over the energy range above 30 eV <112,113,115> seem to agree very well with present measurements when a reasonable cascade contribution of 40%-50% <129> is assumed. But their revised excitation cross sections at energies below 20 eV are almost the same as our measured emission cross sections. If 30% cascade contribution is assumed for this transition below 20 eV, present measurements for the emission cross sections of the OI 130.3 nm indicate that the revised excitation cross sections of Gulcicek and Doering <115> below 20 eV may be overestimated by a factor of 1.4-1.8. It is also noted that their revised cross sections below 20 eV are a factor of 1.6 larger than the calculations of Julienne and Davis <129>, and a factor of 1.3 larger than the calculations of Rountree and Henry <124>. Gulcicek, Doering and Vaughan <116> measured the direct excitation cross section of the 3p $^3P$ state (major cascade contributor to the 3s $^3S^0$ state, subsequently to the OI 130.3 nm emission). Their results indicated that this excitation function was fairly sharply peaked at low energy near 20 eV. Our measured emission cross sections also suggest a larger cascade contribution at low energies compared with the theoretical excitation cross sections (see Figure 8-8), at energies over 20 eV.
The only other emission cross section measurements for the OI 130.3 nm multiplet are those of Zipf and Erdman <83>. These are shown in Figure 8-8. The agreement between present results and Zipf and Erdman's is very good at electron energies above 30 eV, considering the errors involved in both experiments. However, their cross sections at energies below 30 eV are more strongly peaked than the present results. The reason for this is not clear. One possible reason for the difference in shape might be different focusing of the two electron guns and consequent variations in the interaction volumes. In our case, we checked this as discussed earlier. Another possible problem becomes obvious if we consider Equation 8-2. The OI 130.3 nm signal is obtained from $S - S_{on} - (1 - D)S_{off}$ under the same gas pressure and the same electron current with the discharge both on and off. Since emission from atomic oxygen is strong at low energies, while that from molecular oxygen is strong at high energies, it is important to include the dissociation fraction in this equation. Zipf and co-workers simply took their signal from $S - S_{on} - S_{off}$ using a discharge on and off cycle of 30 seconds, and subtracting the data from two schemes automatically. This could cause an enhanced signal at low energies. Further measurements are needed to clear up this discrepancy.

8.3.2 The $2p^3P - 3s^1D^0$ Transition at 98.9 nm

The radiative decay of the $3s^1D^0$ state to the $2p^3P$ ground state of atomic oxygen gives rise to a strong emission at 98.9 nm which is one of the most prominent features in the VUV spectrum of the dayglow and aurora. The $3s^1D^0$ state also branches down to the $3p^3P$ state
emitting a photon of 799.0 nm, and to the $2p^1D$ state resulting in a spin-forbidden transition at 117.3 nm. However, these two branches only account for $1.5 - 2.0 \times 10^{-4}$ of the OI 98.9 nm emission <140>. The first measurement on the OI 98.9 nm emission cross section induced by electron impact on atomic oxygen was carried out by Zipf and Kao in 1983 <141>. However, when their cross section was used in the modeling of the observed intensity of the dayglow, the predicted emission of the OI 98.9 nm feature was an order of magnitude larger than was observed <142>. Later, Zipf and Erdman revised their cross sections, and divided their earlier data by 2.8 in 1985 <83>. Unfortunately, their newly revised cross section for the OI 98.9 nm feature would need a further reduction by multiplying 0.5–0.6 in order to achieve agreement with the analysis of the satellite observations of the OI 98.9 nm dayglow <143>. A recent modeling of the OI 98.9 nm and its branching partner OI 117.3 nm in the terrestrial dayglow also favored a large reduction of their cross section data for the OI 98.9 nm feature <140>.

Vaughan and Doering <113> measured the direct excitation cross sections of the $3s^3D^0$ state by electron impact on atomic oxygen using the electron energy-loss technique in 1987, and found that the energy dependence of their excitation cross section was identical to the cascade-fed emission cross section of Zipf and Erdman's, but with a much smaller magnitude. Later, Gulcicek and Doering <115> revised some of these cross sections by a factor of 1.7 at low energies, but left the high energy cross sections unchanged, this resulted in a different shape in the energy dependence of the excitation cross section for the OI $3s^3D^0$ state. The large emission cross sections of Zipf and Erdman
for the OI 98.9 nm feature were probably due to cascade from the upper states, as pointed out by Gulcicek and Doering [115]. However, a factor of 2 greater than the excitation cross section at 20 eV energy was too large to be explained by cascade alone.

The failure of the emission cross sections of Zipf and Erdman for the OI 98.9 nm feature in modeling the observed intensity of the OI 98.9 nm emission from the satellite observations of the dayglow needs an explanation. Either the cross section data of Zipf and Erdman are overestimated, or the model itself is wrong. The large discrepancy in the excitation and emission cross sections involving cascade contributions to the OI 98.9 nm feature still needs to be resolved. The purpose of present work is to make an independent measurement of the OI 98.9 nm emission cross section by electron impact on atomic oxygen at various energies up to 100 eV, using a different atomic oxygen source (R.F. discharge in this work), and a different parent molecule (NO) for the dissociative production of atomic oxygen.

The present measurement for the OI 98.9 nm emission cross section has been normalized to the emission cross section of the OI 130.3 nm at 100 eV energy obtained earlier. The comparisons between these two atomic oxygen features were made by running the NO spectrum including both features with discharge on and off, integrating over the profiles of these two features, and finally, using Equation (8-2) to obtain signals from electron impact on atomic oxygen for both lines. The advantage of doing so is to eliminate the error caused by fluctuations of the discharge source and subsequently the atomic oxygen number density in
the target beam, and to ensure identical experimental conditions for both features involved in the normalization. Figure 8-9 shows these spectra with discharge on and off. The trapping effect for the OI 98.9 nm feature has been calculated using the known oscillator strengths in Table 8-2 and the geometrical factor obtained in the computer-fitting for the OI 130.3 nm intensity variation with atomic oxygen partial pressure in the target beam. Figure 8-10 gives the calculated curve for the OI 98.9 nm trapping effect.

The presently measured emission cross sections of the OI 98.9 nm feature induced by electron impact on atomic oxygen are listed in Table 8-5, and the curve for the energy dependence of this cross section is shown in Figure 8-11. The only other measured emission cross sections of Zipf and Erdman <83>, and the measured excitation cross sections of Vaughan and Doering <113>, as well as the revised results of Gulcickek and Doering <115>, are presented in the Figure 8-12 for comparison with the present results. The calculated excitation cross sections of Tayal and Henry <119> are also shown in this figure. The measurements of Zipf and Erdman are systematically larger than the present results by about a factor of 2. The reason is probably due to the fact that the trapping effect of resonance lines was neglected in Zipf and Erdman's measurements <83,134>. Because the trapping effect is different for different lines, a comparison made without considering this trapping effect will result in an enhanced cross section for the OI 98.9 nm feature. The degree of the enhancement increases with the atomic oxygen partial pressure in the target beam. For the apparatus used in this work,
FIGURE 8-9: VUV spectrum induced by 100 eV electron impact on NO
FIGURE 8-10: The variation of the OI 98.9 nm emission rate with atomic oxygen partial pressure.
TABLE 8-5

Emission Cross Sections for the OI 98.9 nm multiplet
Induced by Electron Impact on Atomic Oxygen

<table>
<thead>
<tr>
<th>Electron Energy (eV)</th>
<th>Emission Cross Section Present Result</th>
<th>Emission Cross Section Zipf &lt;83&gt;</th>
<th>Excitation Cross Section Doering et al. &lt;113,115&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1.5</td>
<td>3.7</td>
<td>5.41±30%</td>
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<td>4.6</td>
<td>9.66</td>
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<td>12.0</td>
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</tr>
<tr>
<td>30</td>
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<td>5.07±1.9</td>
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<td>5.87±1.4</td>
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<td>14.4</td>
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<td>9.2</td>
<td>14.4</td>
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<td>65</td>
<td>9.0</td>
<td>14.2</td>
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</tr>
<tr>
<td>70</td>
<td>8.7</td>
<td>14.2</td>
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</tr>
<tr>
<td>95</td>
<td>6.9</td>
<td>13.5</td>
<td>4.48±0.9</td>
</tr>
<tr>
<td>100</td>
<td>6.4</td>
<td>13.5</td>
<td></td>
</tr>
</tbody>
</table>

The unit of these cross section data is $10^{-19}$ cm$^2$. The error in the present results is 30%.
FIGURE 8-12: Excitation function of the OI 98.9 nm feature by electron impact on atomic oxygen.
neglect of trapping effect in the comparison would have resulted in an
enhanced emission cross section for OI 98.9 nm by a factor of 2 when
the atomic oxygen partial pressure was about 250 mtorr. It has been
noted that the total gas pressure in Zipf’s measurements <134> was
between 100-1000 mtorr. Thus, a dissociation fraction of 30% could
produce an atomic oxygen partial pressure of 30-300 mtorr. The
microwave discharge used by Zipf et al. was capable of dissociating up
to 50% of the oxygen molecules <115>.

The present results for the OI 98.9 nm feature are about 40% larger
than the cascade-free excitation cross sections of Vaughan and Doering
<113> for 100 eV energy, and the revised value of Gulcicek and Doering
<115> at 20 eV is slightly higher than the present result. Our measured
emission cross sections include direct excitation cross section from the
ground state and cascade contributions from higher states. The 3s' 3D^0
state is populated by the following main cascade transitions: OI
3p' 3F-3s' 3D^0 at 822.2-823.5 nm, OI 3p 3D-3s' 3D^0 at 794.0-795.2 nm,
and OI 3p' 3D-3s' 3D^0 at 382.3-382.6 nm. The cascade contributions to
our measured emission cross sections can not be analyzed properly at
this point because of the lack of cross section information for these
cascade transitions. However, based on recent aeronomic modeling by
Gladstone et al. <140>, cascading to the 3s' 3D^0 state from higher triplet
states probably accounts for no more than 25% of the OI 98.9 nm
emission cross section if Gulcicek and Doering’s results <113,115> for
direct excitation are accurate. Considering the reported 30% errors
involved both in the present work and in that of Doering et al., the
agreement between these two measurements may be considered as good.
However, the electron energy-loss technique used by Doering et al. is not capable of measuring the continuous energy dependence of the excitation cross section (there are only 4 data points for an energy range up to 100 eV), and thus the general shape of their excitation function is not well defined, especially at low energies.

The theoretical excitation cross sections of Tayal and Henry <118> are about 30% lower than our measured emission cross sections at energies above 40 eV, and have a very different energy dependence below 40 eV. Their calculated values start at 20 eV energy and give no indication regarding the cross section variation close to threshold. Tayal and Henry <119> ignored the coupling of the 3s' 3D⁰ state with higher-lying triplet states of F, P and D symmetries in their calculations. These states may be important, and the calculations may be in error, as pointed out in their report <119>. Zipt and Erdman <83> found that cascading from upper triplet states was significant for the dissociative excitation of oxygen molecules, and indicated that cascading might be more significant for the excitation of atomic oxygen. Independent measurements of the cascading transitions are required to check this suggestion and obtain accurate data for direct excitation.

8.3.3 The 2p 3P - 3s' 3P⁰ Transition at 87.8 nm

The normalization for the OI 87.8 nm emission cross section was made by comparison with the OI 130.3 nm feature at 100 eV. The details have been given in the previous section. Experimental conditions were the same as in the OI 98.9 nm measurements. The trapping effect was
calculated using the oscillator strength in Table 8-2, and the geometrical factor obtained in the trapping measurement for the OI 130.3 nm. Figure 8-13 shows the calculated trapping effect for OI 87.8 nm.

Table 8-6 lists our measured emission cross sections for the OI 87.8 nm at various energies up to 100 eV, together with the results of other groups. Figure 8-14 shows our measured excitation function for the OI 87.8 nm feature. The comparison with the cross sections obtained by other groups is given by Figure 8-15. No theoretical calculations are available for comparison. The measured emission cross sections of Zipf and Kao <146> (1986) are systematically larger than the present results by a factor of 3. This discrepancy is most likely due to the calibration of the photon detector. The uncertainties in the secondary standards used for calibrations in this wavelength region are quite high. The $H_2$ band emissions are very weak in this spectral region, any higher noise than signal is capable of causing an error of this size. Therefore, in addition to the $H_2$ molecular branching ratio technique, other secondary standards with strong emission intensities should be used to calibrate the optical system in this spectral region. This has been done in the present measurements (see Figure 5-1 for details). The VUV detector used in Zipf and Kao's work was a 0.3 m McPherson monochromator coupled with a caesium iodide-coated plate of 10 cm$^2$, the high noise level in this combination could cause serious problems when the measured optical signal was weak, $H_2$ vibrational bands used for their calibrations, for example.
FIGURE 8-13: The variation of the OI 87.8 nm emission rate with atomic oxygen partial pressure.
### TABLE 8-6

Emission Cross Sections for the OI 87.8 nm multiplet
Induced by Electron Impact on Atomic Oxygen

<table>
<thead>
<tr>
<th>Electron Energy (eV)</th>
<th>Emission Cross Section</th>
<th>Excitation Cross Section</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present Result</td>
<td>Zipf &amp; Kao &lt;146&gt;</td>
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The unit in these cross sections is 10⁻¹⁶ cm². The error in the present results is 30%.
FIGURE 8-14: Our measured excitation function of OI 87.8 nm.
FIGURE 8-15: Excitation function of the OI 87.8 nm feature by electron impact on atomic oxygen.
The direct excitation cross sections measured by Vaughan and Doering \textsuperscript{114} are about a factor of 2.5 larger than our measured emission cross sections for this feature. This is probably because the \textit{3s} \textit{3P}^0 state of atomic oxygen lies energetically above its ionization threshold, (13.618 eV), and decays via two competing channels: (i) radiative decay emitting a photon at 87.8 nm, (ii) autoionization resulting in a ground state \textit{O}^+ ion and a secondary electron \textsuperscript{114}. Even though the direct excitation cross section for this state is quite large, 10.92\times10^{-18} \text{ cm}^2 at 50 eV measured by Vaughan and Doering \textsuperscript{114}, the OI 87.8 nm emission was hardly observed by satellite and rocket measurements \textsuperscript{145}. This is due to the fact that the OI 87.8 nm emission suffers a huge loss due to trapping and, in turn, the autoionization channel rapidly recycles the OI 87.8 nm photons in the atomic oxygen rich environment, and converts them into \textit{O}^+ ions. Dehmer et al. \textsuperscript{147} (1977) measured the branching ratio of these two decaying channels to be 1.07. Thus, the direct excitation cross section for this state divided by a factor of 2.07 should coincide with the emission cross section of the OI 87.8 nm, if no cascade contributions are involved. The direct excitation cross sections of Vaughan and Doering \textsuperscript{114} divided by 2.07 are about a factor of 1.3 higher than our measured emission cross sections at 30 eV, 50 eV and 100 eV. Considering the errors involved in the measurements of the branching ratio, and the cross sections, this level of agreement is very good and suggests that any cascade contribution to the 87.8 nm feature is small or negligible.

8.3.4 The 2\textit{p} \textit{3P} - 3\textit{d} \textit{3D}^0 transition at 102.7 nm
Figure 8-16 shows the trapping effect for the OI 102.7 nm. Since the oscillator strength for this transition is 0.019 <136>, the smallest among the atomic oxygen resonance lines, the trapping effect is not as serious as for the other lines, an almost linear increase of the emission rate with atomic oxygen partial pressure is clearly demonstrated in Figure 8-16. Figure 8-17 shows the present results for the OI 102.7 nm emission cross sections up to 100 eV. Figure 8-18 shows the comparison with the measured emission cross sections of Zipf and Erdman <83>, and the measured excitation cross sections of Vaughan and Doering <114>, as well as the theoretical excitation cross sections of Tayal and Henry <119> and of Smith <128>. Table 8-7 lists the presently measured emission cross sections at various energies up to 100 eV.

The agreement between our results and those of Zipf and Erdman <83> is good over the a large energy range, except at energies below 25 eV where their results are slightly higher than the present results. However, the trapping effect was neglected by later authors, the results of Zipf and Erdman <83> should be re-evaluated accordingly. The measured excitation cross sections of Vaughan and Doering <114> and the theoretical excitation cross sections of Smith <128> are almost identical to our measured emission cross sections. The theoretical excitation cross sections of Tayal and Henry <119> are somewhat larger and have a different energy dependence. The fairly close agreement between the excitation and emission cross sections implies a negligible cascade contribution to the OI 102.7 nm emission. Figure 8-3 indicates that the major cascade contributions to 3\(d^3D^0\) excitation would be from the \(nf^3F\) states. Excitation of these from the ground 2\(p^2P\) state would

-175-
FIGURE 8-16: The variation of the OI 102.7 nm emission rate with atomic oxygen partial pressure.
FIGURE 8-17: Our measured excitation function of OI 102.7 nm.
FIGURE 8-18: Excitation function of the OI 102.7 nm feature by electron impact on atomic oxygen.
### TABLE 8-7

Emission Cross Sections for the OI 102.7 nm multiplet
Induced by Electron Impact on Atomic Oxygen

<table>
<thead>
<tr>
<th>Electron Energy (eV)</th>
<th>Emission Cross Section</th>
<th>Excitation Cross Section</th>
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The unit for the cross section data is $10^{-18}$ cm$^2$. The error in the present results is 30%.
involve transfer of two units of angular momentum, a rather improbable process. It is not clear why the 102.7 nm feature is cascade-free whereas the 98.9 nm has a relatively large cascade component. Further experiments and theory are needed to clarify this point.

8.4 CONCLUSIONS

The absolute emission cross sections for atomic oxygen resonance transitions at 130.3 nm, 102.7 nm, 98.9 nm and 87.8 nm following electron impact on atomic oxygen have been established for impact energies \( u_r \) to 100 eV. Present results agree very well with the direct excitation cross sections by Doering et al. <111-115> for all the features measured at energies above 30 eV, when cascade contributions are properly allowed for. The revised excitation cross sections at energies below 20 eV of Doering et al. <115> are similar in magnitude to our measured emission cross sections. The trapping effects have been demonstrated to be extremely important for the evaluation of the optical measurements on the atomic oxygen resonance lines. It has been shown that neglect of the trapping effects can result in "enhanced" cross sections. This is probably the reason for the anomalously large cross sections for the OI 98.9 nm and OI 87.8 nm features as measured by Zipf et al. <83,146>. Present emission cross sections for the OI 98.9 nm feature are about 40% larger than the direct excitation cross sections of Vaughan and Doering <113,115>, while our emission cross sections for the OI 102.7 nm are almost identical to the excitation cross sections of Vaughan and Doering <114>. If both measurements are accurate, cascade must be more important for the OI 98.9 nm emission. Concerning the OI 87.8 nm
emission, the much larger excitation cross sections of Vaughan and Doering <114>, than present emission cross sections, indicate a significant autoionization depopulation of the $3s^2 \, 3p^0$ state. This is important in the ion chemistry of the thermosphere, as pointed out by Zipf and Kao <146>, since this autoionization process produces a ground state $O^+$ ion rather than a metastable $O^+$ ion <114,146>. The emission cross section of the OI 130.3 nm at 100 eV impact energy has been established to be $7.7 \times 10^{-18} \text{cm}^2 \pm 25\%$ in 22 separate determinations. This value is 20% lower than the reported emission cross section of Zipf and Erdman <83>, and 20% higher than the cascade-free excitation cross section of Vaughan and Doering <111,112,113,115>. Differences with the emission cross sections of Zipf and Erdman <83> tend to increase as the energy is reduced below 30 eV. The slightly higher excitation cross sections of Vaughan and Doering at energies below 20 eV may indicate a less significant cascade in the low energy range.
APPENDIX

Many channels can contribute to the emission rate of a particular radiation in the emission cross section measurement. Direct excitation to the excited state (emit a photon under study via radiative decay) from the initial state target (usually ground state) is proportional to the emission rate for the radiation involved. The direct excitation cross section refers to this particular process. Higher levels also contribute to the emission rate of the radiation under study by cascading into the related excited level involved. This process provides a cascade contribution to the emission cross section measured. If more than one decaying channel is available for the excited state discussed above, the branching ratio of this particular radiation must be included in the emission cross section evaluation. Figure A-1 shows these contributing channels and the branching ratio involved. Mathematically, the emission cross section \( Q_{\text{em}} \) can be expressed as the following:

\[
Q_{\text{em}} = B(Q_{\text{xsc}} + Q_{\text{cas}}) \tag{A-1}
\]

Where, \( B \) is the branching ratio for the radiation measured; \( Q_{\text{xsc}} \) is the direct excitation cross section; and \( Q_{\text{cas}} \) is the cascade contribution.

 Usually, the emitted photons are polarized. The measured emission cross section must be corrected for this effect if a measurement is made at a right angle to the electron beam direction (see Chapter II for detail). If the polarization effect is unknown, measured emission cross section is
called the apparent emission cross section. Sometimes the radiation is polarization-free, no correction is needed. In this case, measured emission cross section is the same as Equation (A-1).

FIGURE A-1: Schematic of direct & cascade contributions to a particular emission feature.
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VITA AUCTORIS

I was born in Benxi, Liaoning province of the People's Republic of China in March 23, 1957. My primary and high school education was carried out in my hometown, a beautiful mountain city with more than half a million population. In March, 1978, I began my college education at the largest university of the Liaoning province, Northeast University of Technology in the province's capital city, Shenyang with a metropolitan population of about four million. In the second year of my college education, I was honored as the excellent student of the year in the university. During my senior year in the Department of Physics, I was offered a faculty position as an assistant lecturer by the department. I accepted the offer and became a faculty member (assistant lecturer) of the department right after graduation with a B.Sc. degree in Feb 1982. In late 1983, I passed the national entrance examinations for M.Sc. degree in physics with top scores among young assistant lecturers in the Northeast University of Technology which later granted me a leave with pay for my pursuit of a M.Sc. degree in Physics. To get some experience in undergraduate teaching, I was given a chance to teach an undergraduate course, "experimental Physics", and to do some research at the same time. In early 1986, I successfully defended my M.Sc. thesis (and a year later the official diploma was issued when I was doing my second M.Sc. degree at the University of Windsor, Canada). I came to Canada in Dec. 1986, and began my M.Sc. program in physics at the University of Windsor under the supervision of Professor J.W. McConkey. I officially got this M.Sc. degree from the University of Windsor in Oct.
1988, and started my Ph.D research right away under the supervision of Professor J.W. McConkey. During my studies at the University of Windsor, I was granted a University of Windsor Postgraduate Scholarship for the maximum-allowed four continuous years from 1987 to 1991, and a Summer Research Scholarship in 1991 when I was finishing my Ph.D degree.
PUBLICATIONS AND CONFERENCE PRESENTATIONS


