Production and detection of metastable atomic oxygen.

Lance Richard. LeClair
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Production and Detection of Metastable Atomic Oxygen

by

Lance Richard LeClair

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

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ABSTRACT

The metastable species O(^1S) has been observed following the dissociation of O_2, N_2O, and CO_2 molecules by pulsed electron impact. A crossed beam apparatus was used to obtain time-of-flight spectra of the fragments. A novel detector which consists of a layer of freshly deposited Xe was employed. O(^1S) atoms impinging on the surface quickly (~1µs) form XeO* excimers which rapidly decay (~100ns) producing easily detected photons. In the case of O_2 and N_2O present results indicate that this method is sensitive solely to O(^1S) with high quantum efficiency. Other ground state or metastable fragments (such as O(^3P), O(^1D), O(^5S*), or N_2(A^3Σ_u^+)) have not been detected. In the case of CO_2, the Xe layer is sensitive to O(^3S) and the metastable CO(a^3Π). Low resolution optical spectra of the emissions which follow the arrival of O(^1S) at the Xe layer reveal bands at 375, 550, and 725 nm; while CO(a^3Π) fragments impinging on the layer produce emissions below 350 nm. Time-of-flight and released kinetic energy spectra for all target gases at various electron impact energies are presented together with excitation functions from threshold to 1000 eV. These have been made absolute using a Bethe-Born calibration technique for O(^1S) from N_2O. For O(^1S) from O_2 and CO_2, the data are calibrated relative to N_2O. Maximum cross sections for O(^1S) production are 2.25 × 10^{-17} cm^2 at 45 eV, 2.08 × 10^{-18} cm^2 at 80 eV, and 1.68 × 10^{-17} cm^2 at 50 eV, for N_2O, O_2, and CO_2 targets respectively. The cross section for CO(a^3Π) production from dissociative excitation of CO_2 has a maximum of 2.8 × 10^{-16} cm^2 at 25 eV.
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# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>1. INTRODUCTION AND MOTIVATION</td>
<td>1</td>
</tr>
<tr>
<td>2. TIME-OF-FLIGHT SPECTROSCOPY</td>
<td></td>
</tr>
<tr>
<td>Method</td>
<td>7</td>
</tr>
<tr>
<td>The Dissociation Process</td>
<td>10</td>
</tr>
<tr>
<td>Systematic Errors</td>
<td>14</td>
</tr>
<tr>
<td>Excitation Functions</td>
<td>18</td>
</tr>
<tr>
<td>Angular Distribution of the Fragments</td>
<td>20</td>
</tr>
<tr>
<td>Identification of Fragments</td>
<td>21</td>
</tr>
<tr>
<td>3. CALIBRATION OF THE EXCITATION CURVES</td>
<td></td>
</tr>
<tr>
<td>The Concept of Collision Cross Section</td>
<td>26</td>
</tr>
<tr>
<td>The Bethe-Born Approximation</td>
<td>28</td>
</tr>
<tr>
<td>Calibration by the Relative Flow Technique</td>
<td>35</td>
</tr>
<tr>
<td>4. EXPERIMENTAL DETAILS</td>
<td></td>
</tr>
<tr>
<td>The Vacuum System</td>
<td>40</td>
</tr>
<tr>
<td>The Electron Gun and Gas Jet</td>
<td>43</td>
</tr>
<tr>
<td>The Detector</td>
<td>49</td>
</tr>
<tr>
<td>Data Acquisition</td>
<td>54</td>
</tr>
<tr>
<td>5. THE XENON LAYER METASTABLE DETECTOR</td>
<td></td>
</tr>
<tr>
<td>Historical Background</td>
<td>61</td>
</tr>
<tr>
<td>Preparation of the Xenon Surface</td>
<td>65</td>
</tr>
<tr>
<td>Factors Affecting Detector Performance</td>
<td>66</td>
</tr>
<tr>
<td>Spectra of XeO⁺ Emissions and Mechanism of Light Production</td>
<td>72</td>
</tr>
<tr>
<td>6. THE RESULTS OBTAINED FROM NITROUS OXIDE</td>
<td></td>
</tr>
<tr>
<td>Review of Earlier Work</td>
<td>80</td>
</tr>
<tr>
<td>Time-of-Flight and Released Kinetic Energy Spectra</td>
<td>86</td>
</tr>
<tr>
<td>Appearance Potential and Calibrated Excitation Function</td>
<td>96</td>
</tr>
<tr>
<td>Chapter</td>
<td>Pages</td>
</tr>
<tr>
<td>----------------------------------------------------------------------</td>
<td>-------</td>
</tr>
<tr>
<td>7. THE RESULTS OBTAINED FROM OXYGEN</td>
<td></td>
</tr>
<tr>
<td>Review of Earlier Work</td>
<td>106</td>
</tr>
<tr>
<td>Time-of-Flight and Released Kinetic Energy Spectra</td>
<td>112</td>
</tr>
<tr>
<td>Appearance Potential and Calibrated Excitation Function</td>
<td>120</td>
</tr>
<tr>
<td>Identification of Parent O$_2$ States Responsible for the TOF Spectra</td>
<td>130</td>
</tr>
<tr>
<td>8. THE RESULTS OBTAINED FROM CARBON DIOXIDE</td>
<td></td>
</tr>
<tr>
<td>Review of Earlier Work</td>
<td>134</td>
</tr>
<tr>
<td>Time-of-Flight and Released Kinetic Energy Spectra</td>
<td>138</td>
</tr>
<tr>
<td>Appearance Potentials and Calibrated Excitation Functions</td>
<td>145</td>
</tr>
<tr>
<td>9. CONCLUSIONS</td>
<td>154</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>158</td>
</tr>
<tr>
<td>VITA AUCTORIS</td>
<td>163</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction and Motivation

The answer to the question of motivation for this work lies in the luminescent draperies, arcs, patches, and rays of many hues that can bring a numinous sense to the black arctic sky; the Northern Lights. Eather (1980) has produced a very readable and thoroughly enjoyable account of attempts to understand the mechanism behind the Aurora Borealis and Australis from ancient times up to present. More detailed explanations are found in the texts by Vallance-Jones (1974) and Chamberlain (1961). However, it must be noted that auroral research is an ongoing endeavour which continually brings about new information as well as revisions to the old.

In the visible region of the spectrum, the brightest features of the Aurora originate from transitions in ionized molecular nitrogen in the blue, and atomic oxygen in the green and red. There are also several atomic nitrogen and hydrogen
lines. An excellent spectrum of the aurora in colour is found on page 169 of Eather's book. The relative intensities of features in auroral spectra in the visible region and beyond depend on many factors, but an explanation for this is best left for the texts cited earlier.

Laboratory based auroral research is usually concerned with examining the excitation processes responsible for the emissions observed in auroral spectra. For example, many of the transitions of atomic oxygen observed in the aurora (see figure 1.1) have been observed in experimental studies of dissociative excitation of O$_2$ by electron impact (e.g. see the review article by Zipf, 1984). Electron impact is the dominant excitation mechanism in the aurora, either directly or indirectly.

![Figure 1.1](image)

**Figure 1.1**  Energy level diagram of OI showing the transitions that have been observed in the aurora or the airglow. The metastable transitions are indicated by a dot.
The prominent green line in the aurora ($\lambda=5577$ Å) arises from the transition between the $^1S$ and $^1D$ metastable states of atomic oxygen. Since the line is so bright, investigations of the excitation mechanism responsible have been ongoing for years, and are often a source of controversy.

According to Rees (1989), because of the high density of atomic oxygen at altitudes where the aurora occur (most often at $\sim100$ Km or higher), the favoured dominant production mechanism for O($^1S$) is a two step process. Molecular nitrogen is first excited to the metastable A state by electron impact,

$$e + N_2(X^1\Sigma_g^+) \rightarrow e' + N_2(A^3\Sigma_u^+) ,$$  \hspace{1cm} (1.1)

and is then quenched by collision with O($^3P$) to give O($^1S$),

$$N_2(A^3\Sigma_u^+) + O(^3P) \rightarrow N_2(X^1\Sigma_g^+) + O(^1S) .$$  \hspace{1cm} (1.2)

Support for Rees' conclusion is based on the afterglow experiments of Piper (1982), and De Souza et al. (1985) who have measured a quantum yield of $\sim80\%$ for (1.2). However, the values deduced from auroral models vary from 20\% (Gattinger et al., 1985) to 1\% (McDade and Llewellyn, 1984). Therefore the importance of this two step process is still disputed (Llewellyn, 1993).

Another significant mechanism is electron impact excitation of O($^3P$) to O($^1S$). Recently, two absolute cross section measurements for that process have been made (Doering and Gulcicek, 1989; and Shyn et al. 1986), while extensive calculations have been available for years (Henry et al. 1969). Dissociative recombination of O$_2^+$ is a minor contributor (in the aurora), but is still the subject of much experimental and
theoretical work (Zipf, 1980; Guberman and Guisti-Suzor, 1991) because of its importance in the airglow. Production of O(1S) from ion-atom interchange reactions,

\[ \text{N}^+ + \text{O}_2 \rightarrow \text{NO}^+ + \text{O}(1S) \]  

(1.3)

\[ \text{O}_2^+ + \text{N} \rightarrow \text{NO}^+ + \text{O}(1S) \]  

(1.4)

are possible sources of O(1S), but laboratory measurements provide little support (Rees, 1989).

Another source of O(1S) is from dissociative excitation of O_2 by electron impact,

\[ e + \text{O}_2 \rightarrow e' + \text{O} + \text{O}(1S) \]  

(1.5)

No quantitative theoretical or experimental work has been published on this mechanism, but it is not expected to be dominant for the following reason (Vallance-Jones, 1974). Since the number density of O_2 is less than a fifth of that for N_2, and the intensity of the 5577 Å line is greater than or equal to the 3914 Å band from the (0,0) transition of the 1st negative bands of N_2^+, then if (1.5) were the dominant mechanism, its cross section would have to be greater than 5 times the cross section for the electron impact collision on N_2 which produces the 3914 Å band. Thus, the dissociative excitation mechanism (1.5) is not expected to be very significant.

However, the arguments of Vallance-Jones are based on maximum cross section values. Since these occur at rather high electron impact high energies (>50 eV), and since the auroral electron flux rises steeply towards lower energies (Rees, 1989), and since the threshold for 3914 Å production is a few electron volts
higher than for $O(^1S)$ production, it is not inconceivable that process (1.5) might still play an important role. Clearly, knowledge of this collision cross section for a wide range of electron impact energies would be important to aurora models.

There are many absolute cross section measurements for the production of excited states of atomic oxygen following dissociative excitation of $O_2$ by electron impact, and these have been summarized by Zipf (1984). However, investigations of the $O(^1S)$ state are made difficult by its long lifetime ($\tau \approx 0.8s$, Itikawa and Ichimura, 1990). Thus any $O(^1S)$ atoms produced de-excite via collisions with the vacuum chamber walls. Most detection methods rely on buffering the metastable atoms from the walls by using high pressure rare gases such as He, as first observed by McLennan and Shrum (1925), or by lifetime shortening through excimer formation with high pressure Kr or Xe gases, (Cooper et al. 1961; Simmons et al. 1979). Unfortunately, these indirect methods can not be used to obtain important information such as absolute excitation cross-sections, or potential curves for the excited molecular states that produce $O(^1S)$.

Previous attempts to detect $O(^1S)$ by other techniques such as Auger emission from a low work function surface (Gilpin and Welge, 1971; Allcock, 1975), by a chemi-ionization process (Stone et al., 1976), or by detection of inelastically scattered electrons, were limited by a lack of discrimination against other metastable atomic or molecular species or ground state $O(^3P)$ and generally suffered from poor signal to background ratios.
Kiefl et al. (1983) used a time of flight (TOF) technique with a unique detector in order to observe O(\(^1\)S) following electron impact on O\(_2\). They measured relative extinction cross sections for O(\(^1\)S) with various gases, but did not report any excitation cross sections. The novel detector, which they developed, consisted of a layer of Xe freshly deposited on a cryogenically cooled (70K) surface. O(\(^1\)S) atoms impinging on the surface form excimers with Xe which quickly decay. This is a natural extension of the high pressure gaseous detection technique mentioned above.

In this present work, a crossed beam apparatus incorporating a refinement of the Xe surface detector was constructed (chapter 4) to carry out detailed studies of O(\(^1\)S) production following electron impact dissociation of molecules. Time-of-flight spectroscopy (chapter 2) was used to acquire kinetic energy distributions of the O(\(^1\)S) fragments following the break up of N\(_2\)O, O\(_2\), and CO\(_2\) (chapters 6, 7, and 8, respectively). Cross-sections for the production of O(\(^1\)S) as a function of impact energy were made absolute using the Bethe-Born approximation together with a relative flow technique (see chapter 3). Low resolution optical spectra of the Xe-O(\(^1\)S) emissions from the Xe surface are presented as well as a detailed discussion of the detector's operation and its absolute sensitivity (chapter 5).

One goal of this work is to develop this O(\(^1\)S) detector for studies of aeronomically important reactions involving O(\(^1\)S). Some aspects of this work have been presented at various conferences, LeClair et al. (1990, 1991, 1992) and a brief report of some of the N\(_2\)O data was given by LeClair et al. (1992a). The work on O\(_2\) is in press (LeClair and McConkey, 1993).
Chapter 2

Time-of-Flight Spectroscopy

I. Method

Since the 1960's, time-of-flight (TOF) or translational spectroscopy has been a useful method to study electron or photon impact dissociation (EID or PID) of molecules. In a typical TOF experiment, a short pulse of electrons (or photons) collides with a target beam. A metastable detector is placed at a distance, $D$, from the collision region defined by the intersection of the two beams. When the pulse is on, the resulting excitation of the target molecules produces prompt photons which are detected (metastable detectors are usually sensitive to photons as well) and serve to mark the zero time of the TOF scale. When the pulse is off, the metastable fragments (either neutrals or ions) arrive at the detector with a distribution of flight
times, \( f(t) \). These distributions are called TOF spectra and are used to determine the kinetic energies of the fragments released by dissociation. This information is useful in understanding chemical reactions with fast fragments, such as those which take place in the upper atmosphere. TOF spectra also provide information about molecular structure since they can be used to construct the internuclear potential curve (surface) responsible for the dissociation.

A summary of past TOF experiments will not be presented here, but many of them will be referred to during the course of this report. One short-coming of TOF experiments is that they all involve the detection of energetic metastable particles. With the single exception of Stone et al. (1976), there are no TOF spectra reported for ground state neutral fragments released from EID or PID of molecules. Because of their lack of internal excitation energy and their (usually) low kinetic energies (<10 eV) they cannot trigger conventional Auger detectors.

An obstacle in TOF spectroscopy is the identification of the metastable states of the fragments which reach the detector, and, in the case of heteronuclear molecules, identification of the mass of the fragment. This problem will be partly addressed in section VI of this chapter. For the following discussion, it is assumed that the mass of the detected fragment is known.

TOF spectra are readily converted to a fragment kinetic energy distribution \( F(FKE) \) using \( FKE = \frac{1}{2} m(D/t)^2 \) where \( FKE \) is the kinetic energy of the detected fragment, \( m \) its mass, and \( t \) the time-of-flight of the fragment. Since the area under the TOF distribution \( f(t) \) must be equal to the area under \( F(FKE) \), then
\[ f(t) dt = -F(FKE) dFKE, \]  
(2.1)

and it follows that

\[ F(FKE) = \frac{t^3}{md^2} f(t) . \]  
(2.2)

If a diatomic molecule undergoes dissociation, then, from the conservation of momentum, the released kinetic energy (RKE) of the dissociation is

\[ RKE = \frac{M}{m'} FKE \]  
(2.3)

and its distribution, \( F(RKE) \), is given by

\[ F(RKE) = \frac{m'}{Mm} \frac{t^3}{D^2} f(t) = \frac{m'}{M} F(FKE) \]  
(2.4)

where \( m' \) is the mass of the undetected fragment, and \( M = m + m' \) is the mass of the parent molecule. Care must be taken when interpreting the resulting FKE or RKE spectra as the \( t^3 \) factor can cause them to diverge at low values of energy due to background present in experimental data. The RKE distribution can be viewed as a "reflection" of the ground state wavefunction of the nucleus in the repulsive potential curve which brought on the dissociation. To see this, the mechanism of molecular dissociation must first be considered.
II. The Dissociation Process

According to the Franck-Condon principle, when a molecule undergoes a transition between electronic states, whether by absorption of energy following electron or photon impact, or by photon emission, then the positions and relative velocities of the nuclei of the molecules are virtually unchanged during the transition (Bransden and Joachain, 1983). This is simply a consequence of the fact that electrons are so much lighter than the nuclei, and the wave function for the entire molecule can be separated into the electron wavefunction and the nuclear wavefunction (Born-Oppenheimer approximation).

Consider the dissociation of a hypothetical diatomic molecule AB. The potential curve for its ground electronic state is shown in figure 2.1(a), and is labelled X. The minimum in the curve for state X results in a bound molecular state. A second curve labelled Y represents a higher electronic state of the molecule which is repulsive, and at large internuclear distances the molecule separates into atoms A and B* where B* is a metastable state of B. (It should be understood that this is for the sake of argument. Repulsive molecular states are not always from some combination of excited and ground state atoms. It is entirely possible for two ground state atoms to form repulsive states, or, for excited atoms to form bound molecular states). The curve drawn in the potential minimum of state X is the ground vibrational wave function (v=0) that represents the probability distribution function of the relative distances between the nuclei.
Figure 2.1 Potential curves for hypothetical diatomic molecule AB to illustrate (a), dissociation from a purely repulsive state, and (b), dissociation from the repulsive wall of a bound upper state.

Figure 2.2 Released kinetic energy spectra for dissociation processes (a) and (b) in figure 2.1.
Suppose that at the moment of a collision with an electron, the nuclei are separated by a distance \( r' \) shown in the diagram and enough energy is absorbed from the collision to cause a transition to state \( Y \). It will take place along the vertical dashed line (following the Franck-Condon principle). Then the nuclei of \( A \) and \( B \) will separate with a released kinetic energy equal to \( E' \), into the atomic states \( A \) and \( B' \). If, in the instance of a second collision, the relative position was \( r'' \), then the transition would proceed vertically along the dashed line to the upper state, and the RKE would be \( E'' \). The region spanned by the \( v=0 \) wavefunction in the \( X \) state (approximated by the two dashed lines) defines the Franck-Condon region.

For many electron collisions that result in dissociation from state \( Y \), an RKE distribution would develop, which is shown in figure 2.2(a). The positions of \( E' \) and \( E'' \) are indicated. The shape of the distribution arises from the "reflection" of the \( X(v=0) \) nuclear wavefunction in the Franck-Condon region by the potential curve of upper state \( Y \). A dissociation process like the one depicted in figure 2.1(a) is described as dissociation from a purely repulsive state. Such processes always have an RKE distribution illustrated schematically by figure 2.2(a).

Another such process is illustrated in figure 2.1(b). In this example, the upper state \( Y \) has a potential well which partially overlaps the Franck-Condon region. If there is a vertical transition to the upper state at a separation \( r' \), then no dissociation will take place. Instead, some vibrational level of the upper state will be populated. If a vertical transition takes place along the dotted line, then the two fragments \( A \) and \( B' \) will have no relative velocity and the released kinetic energy is
zero. The only transitions which lead to dissociation will take place at internuclear distances to the left of the dotted line. One such transition is indicated at r".

This second type of process is called dissociation from the repulsive wall of a bound state. It has an RKE distribution depicted in figure 2.2(b) and is characterized by a finite value of \( F(RKE) \) at zero kinetic energy. There are varying degrees of this second type of process, depending upon the amount of overlap between the potential well of upper state \( Y \) and the Franck-Condon region of \( X(v=0) \).

In the event of a complete overlap, then, of course, dissociation does not take place, unless the upper state potential curve crosses another which is repulsive. In this case the molecule can undergo an intersystem crossing to the overlapping state, and dissociate. This process is called pre-dissociation.

With regard to the dissociation processes illustrated by figure 2.1 (a) and (b), it is possible to construct a qualitative potential curve for the repulsive state in the Franck-Condon region using the measured \( F(RKE) \) distribution. Such information is useful to theorists in order to check their calculations of potential curves. However, in order to do this, the threshold energy for the dissociation channel under study must be measured (section IV). This will locate the potential curve of the repulsive state with respect to the lowest vibrational level of the ground electronic state, assuming that only the \( v=0 \) state is populated in the target molecules. The assumption is valid at room temperatures. An analytical method for obtaining the repulsive portion of the potential curve from \( F(RKE) \) is described by Zipf (1984).
For dissociation of polyatomic molecules, for example ABC, the processes just described still apply as long as there are only two fragments, say AB and C. However, the intermolecular curves drawn in figure 2.1 should be represented by surfaces. Furthermore, analysis of the RKE spectra is complicated because it is possible for the molecular fragments to be vibrationally and rotationally excited. That is, the potential energy of the dissociating state is partitioned into translational, rotational, and vibrational energy of the fragments. When this occurs, there can be an appreciable fraction of detected fragments with very low kinetic energies. It is no longer possible to deduce the repulsive surface responsible for the dissociation from the RKE spectrum.

There is also the possibility of total fragmentation occurring, e.g. ABC → A+B+C. This can also result in a significant fraction of metastable fragments with near zero kinetic energy. Again, it is impossible to deduce the potential surface responsible.

III. Systematic Errors

Several sources of systematic error occur in TOF spectroscopy which can lead to a degradation of the TOF spectra obtained.
(1). Finite Pulse Width

The effect of the width of the pulse of electrons, $\Delta t$, is to broaden TOF spectra. Usually, the zero of the TOF scale is taken at the center of the electron pulse. This results in a smearing of the released kinetic energy scale given by

$$\frac{\Delta RKE}{RKE} = \frac{2 \Delta t}{t} . \quad (2.5)$$

Thus, the broadening increases at short flight times. For example, in chapter 7 the TOF spectra of O atoms from EID of O$_2$ show an appreciable amount of signal at 25 $\mu$s, where $RKE = 18.8$ eV. The uncertainty due to the 1 $\mu$s wide electron pulse is therefore $\pm 1.5$ eV, but at 42 $\mu$s where the TOF spectra show a maximum, it is only 0.3 eV.

(2). Thermal Energy Spread of the Parent Molecules

The effect of the velocity distribution of the parent molecules is to add or subtract a velocity component to the metastable fragments. The resultant spread in the RKE distribution is given by (Zipf, 1984)

$$\Delta RKE = 2\sqrt{2E_{th}RKE} . \quad (2.6)$$

where $E_{th}$ is the average thermal energy of the parent molecules. As with the effect of finite pulse width, the uncertainty is larger at higher RKE. Its effect can be reduced by using a crossed beam arrangement where the electron beam, target gas beam, and the detector are mutually orthogonal. However, one problem with this is
that very slow metastable fragments with velocities comparable to that of the parent molecule may miss the detector altogether.

(3). Recoil effects.

The electrons impart some momentum to the parent molecule. Experiments and analysis have shown that this is a negligible effect for heavier molecules such as N₂ or larger where a 20 eV electron impact results in a RKE spread of 0.1 eV (Zipf, 1984).

(4). Timing and sampling errors.

TOF spectra are usually acquired with multi-channel scalars. The TOF scale is digitized into segments of width Δtₑ. The effect of this width is, at worst, much like the effect of the finite electron pulse width, and so is significant at short flight times or high released kinetic energies. Calibration of the time scale will have a negligible error with the use of stable and accurate electronics.

(5). Detector response time.

The effect of detector response time is to shift the TOF spectrum towards longer flight times. This can have a serious effect on the RKE distribution and on locating the position of the repulsive curve responsible for dissociation. In metastable detectors which rely on Auger emission of electrons following the impact of metastable on a metal surface, the response time is usually negligible. In other
detectors (e.g. Stone et al., 1976), the response time is substantial, and must be measured in order to correct the TOF spectra.

(6). Correction for in flight decay of the metastable.

If the lifetime of the metastable fragment under study is comparable to its time-of-flight, then \( F(RKE) \) is distorted at low energies. If the lifetime is known, then it is possible to correct the TOF spectra (Mason and Newell, 1989). For \( O(1^1S) \) atoms, which are the subject of this paper, the lifetime is nearly a second so the effect is negligible.

(7). Uncertainty in the TOF distance.

The width of the electron beam, and spatial extent of the metastable detector both contribute to the uncertainty in the distance between the origin and termination of the flight path of the metastable, \( \Delta D \). This resulting error in \( RKE \) is

\[
\frac{\Delta RKE}{RKE} = \frac{2 \Delta D}{D} \tag{2.7}
\]

For this experiment the distance \( D \) to the detector is 265 mm. The electron beam width is 1 mm, so its relative contribution to the error in \( RKE \) is negligible. However, the detector (see next chapter) is a surface oriented 45° to the incident metastable. This results in a spread in arrival distances of about ±1 cm, resulting in an uncertainty in the \( RKE \) of about ±8%.
(8). Detection efficiency versus metastable fragment velocity.

In Auger emission detectors, there appears to be little change in the detection efficiency over the velocity range of metastable fragments impacting on the surface. Other types of detectors may exhibit a strong velocity dependence. If this is so, it can sometimes be measured and accounted for (e.g. Stone et al., 1976).

IV. Excitation Functions

TOF experiments can also give the excitation function for the dissociation process under study. If the yield of all (i.e. regardless of flight time) metastables of a particular state are plotted versus electron impact energy then the total excitation function of that species is obtained. In such a curve there can be sharp changes in slope because other metastable production channels become available at higher incident energies. These channels arise either because higher lying molecular states which dissociate to the metastable under study become energetically accessible, or, these higher lying states produce fragments in other excited states which cascade to the metastable being detected. As these additional channels appear, they can give rise to changes in TOF (hence RKE) structure as shown, for example, in the RKE spectra in figure 7.1(a).

It was stated earlier in section II that an RKE spectrum from the dissociation of a diatomic molecule can be used to reconstruct the repulsive portion of the
internuclear curve in the Franck-Condon region. The method for locating the position of this curve can now be described.

![Diagram of potential energy curves](image)

**internuclear separation**

*Figure 2.3* Illustration of internuclear potential curves for diatomic molecule AB and relevant quantities defined in text.

Consider a transition between the bound state X and dissociative state Y of diatomic molecule AB, illustrated in figure 2.3. An apparatus for obtaining TOF spectra can be set by electronic gating so that only fragments within a narrow range of flight times centered around a specific value of released kinetic energy (RKE in the figure 2.3) are counted. If an excitation function is acquired (called a windowed
excitation function), then the threshold for the result will be $E_r$. From the diagram it is clear that

$$E_t = E_A + E_B + E_d + RKE,$$  \hspace{1cm} (2.8)

where $E_A$ and $E_B$ are the excitation energies of the metastable atoms $A^*$ and $B^*$ which result from state $Y$, and $E_d$ is the dissociation energy of the molecule $AB$, in its the ground vibrational state $X(v=0)$ with respect to the separated atoms in their ground states. Substituting equation (2.3) into (2.8) and rearranging, the result is

$$FKE = \frac{m'}{M} (E_t - E_{dl})$$  \hspace{1cm} (2.9)

where $E_{dl} = E_A + E_B + E_d$ is called the dissociation limit. By acquiring the thresholds from several windowed excitation functions for various values of FKE, a plot of FKE versus $E_t$ results in a straight line with slope $m'/M$ with an intercept on the abscissa, $E_{dl}$. Thus the location of the internuclear potential curve in the Franck-Condon region can be found using the sum of the dissociation limit and the minimum released kinetic energy observed from TOF spectra.

V. Angular Distribution of the Fragments.

Direct dissociation of a molecule occurs on a time scale which is fast compared to its rotation. The fragments tend to fly apart in the direction of vibration. Thus, if the molecule has a preferred direction (relative to the incident electron beam) for the initial excitation to occur, an anisotropic distribution of the fragments
can result. This has been analyzed by Dunn (1962), and Zare (1967). Normally, this phenomenon is only significant near threshold and for simple molecules like H₂. At higher impact energies the angular distribution quickly becomes isotropic (e.g. Misakian et al., 1975, for work on CO₂). In this present work, an isotropic distribution has been assumed.

VI. Identification of Fragments

The methods of analyzing TOF spectra in the preceding discussion can only take place if the mass and quantum state of the metastable fragment can be identified. The problem of identification arises because most metastable detectors rely on the Auger emission of electrons following metastable fragment impact on a surface. This will take place as long as the excitation energy of the metastable fragment exceeds the work-function of the surface. The electrons produced are easily detected by a suitable electron multiplier.

In order to identify the fragment, the experimentalist must know all of the possible metastable fragments which could be produced by electron impact on the molecule under study, including metastable states of the molecule itself since it is usually possible for target molecules to reach the detector. For example, the three molecules under study in this paper are N₂O, O₂, and CO₂. The possible metastable fragments that could arise from these are shown in table 2.1, along with their lifetimes, excitation energies, and references.
Table 2.1 Possible metastable states arising from electron impact on N₂O, O₂ and CO₂

<table>
<thead>
<tr>
<th>Target</th>
<th>State</th>
<th>Energy (eV)</th>
<th>Lifetime (s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>N₂O⁺</td>
<td>No metastable N₂O reported.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>N₂(A³Σ⁺)</td>
<td>6.17</td>
<td>1.9</td>
<td>Itikawa et al., 1986</td>
</tr>
<tr>
<td></td>
<td>N₂(W¹Δ⁻)</td>
<td>7.36</td>
<td>4</td>
<td>ibid.</td>
</tr>
<tr>
<td></td>
<td>N₂(a¹Σ⁻)</td>
<td>8.40</td>
<td>0.5</td>
<td>ibid.</td>
</tr>
<tr>
<td></td>
<td>N₂(w¹Δ⁻)</td>
<td>8.89</td>
<td>1.5 × 10⁴</td>
<td>ibid.</td>
</tr>
<tr>
<td></td>
<td>N₂(a¹Π⁻)</td>
<td>8.55</td>
<td>1.15 × 10⁴</td>
<td>ibid.</td>
</tr>
<tr>
<td></td>
<td>N₂(E³Σ⁺)</td>
<td>11.87</td>
<td>1.9 × 10⁴</td>
<td>ibid.</td>
</tr>
<tr>
<td></td>
<td>NO(a¹Π)</td>
<td>4.77</td>
<td>0.16</td>
<td>Zarur and Chiu, 1973</td>
</tr>
<tr>
<td></td>
<td>N(⁴D⁰)</td>
<td>2.38</td>
<td>&gt;8 × 10⁴</td>
<td>Wiese et al., 1966</td>
</tr>
<tr>
<td></td>
<td>N(⁴P⁰)</td>
<td>3.58</td>
<td>&gt;18</td>
<td>ibid.</td>
</tr>
<tr>
<td>CO₂</td>
<td>CO₂⁺</td>
<td>No metastable CO₂ reported.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO(a¹Π)</td>
<td>6.04</td>
<td>9 × 10³</td>
<td>Erdman and Zipf, 1983</td>
</tr>
<tr>
<td></td>
<td>CO(f¹Σ⁻)</td>
<td>~10</td>
<td>8 × 10⁵</td>
<td>Mason and Newell, 1988</td>
</tr>
<tr>
<td></td>
<td>C(¹D)</td>
<td>1.26</td>
<td>&gt;380</td>
<td>Wiese et al., 1966</td>
</tr>
<tr>
<td></td>
<td>C(¹S)</td>
<td>2.68</td>
<td>2</td>
<td>ibid.</td>
</tr>
<tr>
<td></td>
<td>C(⁴S⁰)</td>
<td>4.18</td>
<td>&gt;0.04</td>
<td>ibid.</td>
</tr>
<tr>
<td>O₂</td>
<td>O₂(a¹Δ⁻)</td>
<td>0.98</td>
<td>5300</td>
<td>Bates, 1988</td>
</tr>
<tr>
<td></td>
<td>O₂(b¹Σ⁺)</td>
<td>1.63</td>
<td>12</td>
<td>ibid.</td>
</tr>
<tr>
<td></td>
<td>O₂(c³Σ⁻)</td>
<td>4.05</td>
<td>3.4</td>
<td>Bates, 1989</td>
</tr>
<tr>
<td></td>
<td>O₂(A¹Δ₁)</td>
<td>4.26</td>
<td>1.6</td>
<td>ibid.</td>
</tr>
<tr>
<td></td>
<td>O₂(A³Σ⁺)</td>
<td>4.39</td>
<td>0.10</td>
<td>ibid.</td>
</tr>
<tr>
<td></td>
<td>O(¹D)</td>
<td>1.97</td>
<td>134</td>
<td>Itikawa and Ichimura, 1990</td>
</tr>
<tr>
<td></td>
<td>O(¹S)</td>
<td>4.19</td>
<td>0.74</td>
<td>ibid.</td>
</tr>
<tr>
<td></td>
<td>O(⁴S⁰)</td>
<td>9.15</td>
<td>1.85 × 10⁴</td>
<td>Mason and Newell, 1990</td>
</tr>
</tbody>
</table>
Note that the excitation energies and lifetimes for the molecular metastable states in table 2.1 are given for the lowest vibrational level. Lifetimes can vary widely over the range of vibrational levels for a particular metastable state.

One step towards assigning a TOF structure to a particular metastable is to check for the presence of metastable molecules of the target gas under study. These are easily identified since they travel at thermal energies (in most experimental situations), and, it can be assumed they possess a Maxwell-Boltzmann distribution of velocities. Thus, they will have a most probable time-of-flight given by

$$t_p = \sqrt{\frac{MD^2}{4kT}}$$  \hspace{1cm} (2.10)

where $k$ is Boltzmann's constant, $T$ is the temperature of the gas in the collision region, and $D$ is the distance from the interaction region to the detector. The most probable time of flight corresponds to the maximum in the TOF distribution of the metastable target molecules.

Atomic or molecular metastable fragments which are the product of dissociation generally reach the detector at flight times shorter than that given in equation (2.10). These require more effort in order to achieve a positive identification of their states. It is possible to discriminate against many lower lying metastable states by using a sufficiently high work function Auger detector. It is also advantageous to use two detectors with dissimilar work functions in order to make identification by comparison as in the effort of Barnett et al. (1991). The disadvantage with using Auger emission detectors of low work function for
metastables such as O(1S) is that they tend contribute a lot of background noise due to thermionic emission (Allcock, 1975; Allcock and McConkey, 1976). In addition, low work function surfaces require extremely clean vacuum environments, otherwise they become contaminated, gradually losing their effectiveness (ibid.), unless a means to refresh the surface can be devised (i.e. Gilpin and Welge, 1971).

It is also possible to identify an unknown fragment from the slope of its FKE versus E, graph (equation 2.9) using the procedure discussed by Allcock and McConkey (1978).

Another piece of useful information to aid identification of the detected fragments comes from the shape of the excitation curve. Excitation curves which rise to a maximum at an energy about $5$ times the threshold energy, and then fall off with a $\ln(E)/E$ dependence, are typical of transitions between optically allowed states in the target molecule (see the next chapter). Excitation curves which rise sharply at the threshold and fall off with a $E^3$ dependence are typical of optically forbidden transitions which require an electron exchange in order to occur (Henry et al., 1969). Once the type of transition is established, several choices of dissociating states can then be made. In the case of diatomic or linear polyatomic molecules this information can be used together with the Wigner-Witmer rules on how molecular states correlate to asymptotic atomic states (Herzberg, 1950; 1967) and thus aid identification.

In many cases it is simply not possible to make a positive identification of the fragments, especially for more complex molecules. One way to overcome this
limitation in TOF spectroscopy is to use a method of detection which is selectively sensitive to a particular metastable state of a certain atom or molecule. Stone et al. (1976) partly achieved this with a detector sensitive only to oxygen atoms. However, their detector was unable to discriminate between various metastable states of atomic oxygen and was sensitive to ground state oxygen atoms as well.

The use of resonance enhanced multi-photon ionization appears promising with the work of Schafer et al. (1991) who detected O(1D) atoms following PID of O₂ using an intense U.V. laser beam.

This present work shows how the problems of detector selectivity have been overcome for one particular metastable state. A Xe layer is used to selectively detect O(1S) atoms by XeO excimer conversion. It is a much less expensive solution to O(1S) detection than via multi-photon ionization techniques.
Chapter 3

Calibration of the Excitation Curves

I. The Concept of Collision Cross Section

Excitation functions of metastable atoms are usually recorded as count rates versus electron impact energy in modern experiments. The count rate on the ordinate must be converted to a more practical unit if the data is to be useful to other scientists. Following appropriate calibration, the result is the integral cross section, \( \sigma \). It can be thought of as representing the cross sectional "area" presented by a molecule to an incident electron. If the electron strikes that "area", the molecule will be excited to a state which dissociates to the metastable under study.

The production of metastables can be pictured this way. Consider a current of electrons \( I/e \) (particles per second) traversing an infinitesimal volume element
(thickness = dz, area = dA) of gas at density N (molecules per cm\(^3\)) in the positive z direction. Then the fraction of the current \((dI/I)\) which interacts with the molecules, producing an excitation from the ground electronic state \(\psi_o\) to some dissociating quantum state \(\psi_n\), is equal to the cross sectional area of all the molecules in the volume element for this processes, \(\sigma_n\), over the cross sectional area of the beam. This is expressed as

\[
\left| \frac{dI}{I} \right| = \frac{\text{area of targets}}{\text{area of beam}} = N \sigma_n \, dz . \tag{3.1}
\]

Since the excited state produces a metastable, the magnitude of current loss \((dI)\) equals the emission rate \(d\dot{M}\) of metastables from the volume \(dV = dz \, dA\). That is

\[
d\dot{M} = I N \sigma_n \, dz . \tag{3.2}
\]

If the current is rewritten as the product \(N_e \nu dA\), where \(N_e\) is the concentration of electrons at the location of the volume element \((x,y,z)\), and \(\nu\) is the relative velocity in the center of mass frame, then the microscopic equation for the number of metastables released per second per unit volume per steradian is

\[
\frac{d\dot{M}(x,y,z)}{dV \, d\Omega} = \frac{1}{4\pi} N_e(x,y,z) N(x,y,z) \nu(x,y,z) \sigma_n , \tag{3.3}
\]

where the dependence of each quantity on the coordinate \((x,y,z)\) in the collision volume has been written out explicitly. Note that it has been assumed that the metastable emission is isotropic.

The count rate of metastable particles recorded in an experiment would be determined by integration of (3.3) over the entire collision volume and solid angle.
sustended by the detector. Integrating (3.3) exactly is difficult in practice, but some good approximations can be made. This will be discussed in section III.

However, even assuming that all parameters in (3.3) can be accurately evaluated a problem still remains in that the detection efficiency, \( q \), of any metastable detector needs to be correctly established. The detection efficiency is the ratio of particles counted by a detector to the actual number of particles incident on the detector, and is seldom unity. A measurement of \( q \) is very difficult to obtain in practice.

One way of overcoming the problems of both detector efficiency and of absolute target number density determination is by use of the Bethe-Born approximation.

II. The Bethe-Born Approximation

If the dissociating state is accessed via a dipole allowed transition from the ground state, then it is possible to make a relative excitation function measurement absolute by using the Bethe-Born approximation. This is a calibration method commonly employed by those studying electron impact excitation and ionization of atoms and molecules (Trajmar and Cartwright, 1984). It has been reviewed in great detail by Inokuti (1971), and again by Inokuti et al. (1978). The following shortened derivation is from the former article. Further details can be obtained from the references cited therein.
Suppose an experiment is built so that instead of detecting the metastable fragments following electron impact excitation from $\psi_o$ to $\psi_n$, the electrons scattered after exciting that particular transition are counted. One would do this by an arrangement depicted in figure 3.1, where an electron detector that subtends a solid angle $d\Omega$ is placed at the polar angles $(\Theta, \Phi)$ with respect to the origin. This set up would result in a measurement of the partial differential cross section, $d\sigma_n/d\Omega$, which must be integrated over the polar angles to obtain the integral cross section $\sigma_n$.

![Figure 3.1](image)

**Figure 3.1** Geometry of electron scattering described in the text.

Born (see Bransden and Joachain, 1983) has shown that when a structureless charged particle with relative velocity $v$ in the center of mass frame, that is sufficiently fast, but not relativistic, collides with an atom, inducing a transition to the
The \( n^{th} \) state with energy \( E_n \) and thereby losing some kinetic energy, the differential cross section for the process is given by (in the lowest order)

\[
d\sigma_n = \frac{M^2}{2 \pi \hbar^4} \frac{k'}{k} \left| \int e^{iK \cdot r} \psi_n^* \psi_0 \, dr_1 \cdots dr_Z \, d\Omega \right|^2 \, d\Omega ,
\]

where \( M = M_1 M_2 / (M_1 + M_2) \) is the reduced mass of the colliding system, \( Z \) is the number of electrons in orbit around the atom, \( r \) is the position of the colliding particle with respect to the nucleus, \( r_i \) the position of the \( i^{th} \) orbiting electron, \( \hbar k \) is the momentum of the particle before collision, \( \hbar k' \) is its momentum after, and \( \hbar K = \hbar (k - k') \) is the momentum transfer to the atom. \( V \) is the interaction potential between the impacting particle and the electrons and nucleus of the atom, i.e. it is usually Coulombic, of the form

\[
V = -\sum_{j=1}^{Z} \frac{Qe}{|r-r_j|} + \frac{Z_N Qe}{r},
\]

where \( Z_N e \) is the charge of the nucleus, and \( Q \) the charge of the impacting particle.

If the collision is between an electron and an atom in a gas sample at room temperature, then the reduced mass can be replaced by \( m_e \) and the relative velocity \( v \) in the center of mass frame becomes the electron velocity in the laboratory frame for electron collisions greater than \( -1 \) eV.

Bethe performed the integral in (3.4) by using the fourier transform

\[
\int \frac{e^{iK \cdot r}}{|r-r_j|} \, dr = \frac{4\pi}{K^2} e^{iK \cdot r_j},
\]

Thus (3.4) becomes
\[ d\sigma_n = \frac{4m_e^2e^4}{\hbar^4} \frac{k'}{k} \frac{1}{K^2} |\epsilon_n(K)|^2 d\Omega, \]  

(3.7)

where \( \epsilon_n(K) \) is the matrix element

\[ \epsilon_n(K) = \langle \psi_n | \sum_{j=1}^{Z} e^{iK \cdot r_j} | \psi_o \rangle. \]  

(3.8)

Since the atoms are not in any particular orientation, the differential cross section is symmetric about the z axis, and the quantity \( |\epsilon_n(K)|^2 \) can be replaced by \( |\epsilon_n(K)|^2 \), and \( d\Omega \) by \( 2\pi \sin \theta d\theta = \pi d(K^2)/kk' \). Using \( E = \sqrt{2m_e\gamma} \), and \( W = (\hbar K^2)/2m_e \) (3.7) becomes

\[ d\sigma_n = \frac{\pi e^4}{E W} |\epsilon_n(K)|^2 d(\ln W), \]  

(3.9)

where \( E \) is the electron impact energy, and \( W \) is the recoil energy.

Bethe introduced the quantity known as the generalized oscillator strength which can be expressed in a convenient form as

\[ f_n(K) = \frac{E_n}{K^2 a_o^2 R} |\epsilon_n(K)|^2, \]  

(3.10)

where \( R = 13.606 \text{ eV} \) is the Rydberg unit of energy, and \( a_o = 0.52918 \times 10^{-8} \text{ cm} \) is the Bohr radius. The generalized oscillator strength is a generalization of the spectroscopic quantity known as the optical dipole oscillator strength \( f_n \), given by
\[ f_n = \frac{E_n}{R} |\langle \psi_n | r | \psi_o \rangle|^2, \] 

(3.11)

the last term being the dipole matrix element squared. The optical dipole oscillator
strength defines the magnitude of photo-absorption into the \( n^{th} \) state of the target.
Usually, it can be easily measured from absorption spectra.

Expanding the exponential in (3.8) into a Taylor series, and using the
orthogonality of eigenstates \( \psi_o \) and \( \psi_n \), it can be shown that

\[ \lim_{K \to 0} f_n(K) = f_n. \] 

(3.12)

Thus, at high impact energies, \( E >> E_n \), the energy of the outgoing electron is close
to its incident energy, the scattering takes place mostly in the forward direction, and
the optical dipole oscillator strength can be substituted for the generalized oscillator
strength in (3.9). Equation (3.12) is an important relationship which states that in the
high energy limit, charge particle collisions with atoms simulate photoabsorption.

Following Inokuti (1971), equations (3.9) and (3.10) may be integrated over all
momentum transfer, \( W \), to obtain

\[ \sigma_n = \frac{4 \pi a_o^2}{E} \left[ \frac{R f_n}{E_n} \ln \left( \frac{4 C_n E}{R} \right) + \frac{\gamma_n R}{E} + \mathcal{O} \left( \frac{E_n}{E} \right)^2 \right], \] 

(3.13)

where \( C_n \) is given by
\[ C_n = (\overline{K} a_o R / E_n)^2 \]  \hspace{1cm} (3.14)

in which \( \overline{K} \) is the average momentum transfer for the collision. The quantity \( \gamma_n = -f_n/2 - E_{df n}/4R \) represents an error term in the solution to the integral. For allowed transitions excited by electron impact at sufficiently high energies, i.e. when \( E >> E_n \), the last two terms in (3.13) can be neglected. Thus, for optically allowed transitions excited by electron impact, the integral cross section has a \( \ln(E)/E \) dependence at high impact energies given by

\[ \sigma_n = \frac{4 \pi a_o^2 R^2 f_n}{E E_n} \ln \left( \frac{4 C_n E}{R} \right) \]  \hspace{1cm} (3.15)

So far, the derivation has been concerned with atoms, but the same results apply to molecules. In the case of molecular dissociation, \( \psi_n \) would represent the excited electronic state of the molecule which results in dissociation, producing the detected metastable fragment. The quantum states for molecules are of course described by rotational and vibrational as well as electronic quantum numbers, but given the typical energy resolution of most electron impact experiments, \( \sim 1 \) eV, the excited electronic states are effectively degenerate with respect to the additional quantum numbers. Furthermore, molecular rotation can be considered slow with respect to a fast collision process. Thus, in collision studies, the value obtained for the relative cross section is the average over all orientations of the molecule with respect to the electron beam. In addition, the electron spin has been neglected in the
derivation, as well as exchange effects during the collision. Both of these effects are negligible at high impact energies (Bransden and Joachain, 1983).

Once a relative excitation function has been obtained from experiment (count rate versus electron impact energy), it can be made absolute using (3.15) provided the optical oscillator strength for the transition, \( f_n \), is known. A further necessary condition is that the particular excited state being observed is populated solely by electron collisions on the molecule. If cascade from higher lying states, or collisional transfer of energy from other excited states cannot be neglected, then these processes must be accounted for in the calibration.

The method is to simply plot the product of count rate and electron impact energy versus the natural logarithm of the electron impact energy. This is called a Fano plot (Fano, 1954). At sufficiently high impact energies, a straight line can be fit to the data. Its intercept on the energy axis is \( E_{\text{int}} = R/4C_n \), which determines the constant \( C_n \) for equation (3.15). The integral cross section can then be reliably calculated at high impact energy, without having to know the detection efficiency, or other experimental parameters. This is then used to normalize the rest of the curve.

The accuracy of the technique is limited only by the accuracy with which the optical oscillator strength is known and the accuracy with which \( C_n \) can be established. Since the quantity \( C_n \) appears inside the natural logarithm term in (3.15), an uncertainty in \( C_n \) has only a small effect on the uncertainty of the cross section provided \( 4C_nE/R > 1 \). Thus, the technique has the potential to obtain very accurate cross-section values.
III. Calibration by the Relative Flow Technique.

Once an integral cross section has been established for metastable production from one gas, it can be measured for other gases by comparison under identical experimental conditions. However, in a crossed beam experiment, gases of differing molecular weight will have different flow rates though the capillary tube that directs the gas jet across the electron beam. Hence, some means of determining the relative target gas densities must be employed as a correction factor.

The metastable count rate, \( R_M \), measured by a crossed beam experiment is obtained by integration of (3.3) and multiplying it by the quantum efficiency and an attenuation factor to give

\[
R_M = q \exp[-N_x \sigma_x D] \sigma \frac{\Omega}{4\pi} \int N_e(x,y,z) v(x,y,z) N(x,y,z) \, dV ,
\]  

(3.16)

where \( \Omega \) is the solid angle subtended by the detector. The attenuation factor comes from Beer's Law and is simply a term which accounts for the attenuation of the metastable beam due to collisions with the background gas en route to the detector over the distance \( D \). Its use requires knowledge of the background gas number density, \( N \), and the collision cross section between the metastables and the background gas, \( \sigma_x \). Note that equation (3.16) describes the situation where the loss of metastables due to in flight radiative decay can be neglected.
For a well collimated electron beam, the product $N_e \nu$, which is the microscopic current density $j$, can be replaced by the average current density (in electrons/cm$^2$ sec) expressed as

$$ j = \frac{I}{eA}, \quad (3.17) $$

where $I$ is the current of the electron beam measured by a faraday cup, $e$ the electron charge, and $A$ the cross sectional area of the beam. Equation (3.16) becomes

$$ R_M = \sigma q \exp[-N_x \sigma_x D] \frac{\Omega}{4\pi} \frac{I}{eA} NV. \quad (3.18) $$

where the microscopic number density $N(x,y,z)$ has been replaced by its average value $N$ over the collision volume $V$ formed by the intersection of the electron beam and gas jet.

By taking a ratio of the metastable count rate, $R_m$, from a target gas that has a known cross section, with the same quantity, $R_M'$, for a different target gas at source density, $N'$, and electron beam current, $I'$, the result from (3.18) is

$$ \sigma' = \sigma \frac{R_M'}{R_M} \frac{I}{I'} \frac{N}{N'}, \quad (3.19) $$

which gives an expression for the unknown cross section, $\sigma'$, in terms of the known cross section and other measurable quantities.

Note that in order to obtain (3.19), it has been assumed that the attenuation coefficient is approximately the same for both gases.
For this experiment, the target gas is directed across the electron beam from a capillary tube (see the description of the apparatus in the following chapter) with length $l$ and inner diameter $d$. Upstream of the capillary is a reservoir of gas at a pressure $P$ (the source pressure).

Under so called "molecular flow" conditions, where the mean free path of the target gas is significantly greater than $d$, it is well known that the number density in the interaction region is directly proportional to the source pressure, and the spatial distribution of molecules within the beam is determined by the geometry (the ratio $l/d$) of the capillary (Latimer and McConkey, 1965). Thus, under these conditions, $N/N'$ can be replaced by $P/P'$ in equation (3.19).

As source pressures are increased, it is still possible to normalize data from two gases provided the source pressures behind the capillary forming the beam are such that the mean free paths are identical. If this is so both will have the same spatial distribution function and the so called relative flow technique can be applied. For details, see Trajmar and McConkey (1993) and references therein.

In the present experiment, for reasons of signal intensity, it was necessary to work at quite high source pressures, considerably higher than in the molecular flow regime. A method was therefore devised to relate the average number density in the interaction region at high source pressure to that under molecular flow conditions. The basis of this method was to use the prompt photon signal emitted during the interaction of the electron and gas beams as a monitor of effective gas density.
A filter was used to select a prompt photon wavelength arising from a particular molecular transition. The chosen transition met several criteria. It had a very short lifetime (<100 ns) so that the excited molecules did not drift out of the field of view of the photomultiplier prior to radiating, or become collisionally deactivated. In addition, the particular state was not susceptible to the effects of resonance trapping of radiation which can occur at higher gas densities.

As in equation (3.18), the photon count rate in the molecular flow regime, $R_{mf}$, can be expressed by

$$R_{mf} = q_p \sigma_p \frac{\Omega I}{4\pi eA} N_{mf} V_{mf},$$  \hspace{1cm} (3.20)

where $q_p$ is the efficiency for photon detection, $\sigma_p$ is the cross section for the molecular state which emits the photon, and the subscript mf refers to quantities in the molecular flow region. Taking a ratio between (3.20) and the same expression for a higher source pressure, the result is

$$\frac{R_{mf}}{R} = \frac{N_{mf} V_{mf}}{N V},$$  \hspace{1cm} (3.21)

where $R$ refers to the photon count rate at the higher source pressure.

Next, a plot of the photon count rate versus source pressure is made for the gas with the known cross section for metastable production, and the same is done for the gas with the unknown cross section. By taking ratios of equation (3.21) applied to both gases and rearranging it, one obtains
\[
\frac{N}{N'} = \frac{N_{mf}}{N'_{mf}} \frac{R'_{mf}}{R_{mf}} \frac{R}{R'} .
\] (3.22)

As stated earlier, under conditions of molecular flow where the mean free path for both gases is identical, then

\[
\frac{N_{mf}}{N'_{mf}} = \frac{P_{mf}}{P'_{mf}}.
\] (3.23)

and (3.22) becomes

\[
\frac{N}{N'} = \frac{P_{mf}}{P'_{mf}} \frac{R'_{mf}}{R_{mf}} \frac{R}{R'}.
\] (3.24)

which is substituted into (3.19) to obtain finally

\[
\sigma' = \sigma \frac{I}{I'} \frac{R}{R'} \frac{R'_{M}}{R_{M}} \frac{R'_{mf}}{R_{mf}} \frac{P_{mf}}{P'_{mf}}.
\] (3.25)
Chapter 4

Experimental Details

I. The Vacuum System

A schematic diagram of the entire apparatus is shown in figure 4.1. It was an O-ring sealed vacuum system with four differentially pumped chambers and could reach an ultimate pressure of $2 \times 10^{-7}$ torr. The large cube shaped chamber was evacuated by a 1000 l/s turbo pump (TP) (Varian Model V-1000). An MKS 941 cold cathode gauge provided pressure measurements. This main chamber housed the electron gun (EG) and the target gas jet. A port on the right wall of the large cube chamber led to the detector chamber which housed the cold finger (CF). The electron beam, gas jet, and line of sight to the cold finger were mutually orthogonal.
The electron gun was housed in a differentially pumped T shaped chamber. Electrical connections were made through a ceramic feedthrough on the rear flange of the chamber. It was evacuated by a second 1000 l/s turbo pump (Edwards ETP 160/1000) through a 4 cm diameter pipe which was connected at the bottom of the T shaped chamber. Further details about the design of the electron gun are given below. It was necessary to differentially pump the electron gun because of the corrosive action of O₂ on the hot filament. In preliminary work (Corr, 1987) the
filament was directly exposed to \( \text{O}_2 \) and lasted an average of 8 hours; but with the improved design, filaments have lasted for months.

A small chamber measuring \( 3 \times 2.5 \times 2.5 \) cm contained deflection plates (DP) separated by 1 cm to electrostatically remove ions and electrons and quench Rydberg species. This chamber was evacuated by the same turbo pump used for the electron gun, through a 4 cm diameter tube. Products of dissociation entered this chamber through two defining apertures 2.5 mm in diameter located 2.2 cm and 4.7 cm from the collision region formed by the intersection of the electron and gas beams. Both apertures were blackened with soot to reduce the amount of filament light reaching the photomultiplier. Products leaving the deflection plate chamber went through a third blackened aperture 8 mm in diameter, located 7.3 cm from the electron beam. The third aperture was installed because during operation the cold finger chamber was evacuated through the deflection plate chamber, and it was necessary to limit the pumping speed to reduce the consumption of xenon.

A solid layer of xenon was grown on the tip of the cold finger, oriented 45 degrees to the flight path. The geometry defined the flight path length, \( D \), to 26.6 ± 1.0 cm from the collision region. A gate valve (not shown in figure 4.1) located between the deflection plates and the cold finger was used to isolate the cold finger when there was a need to replace the filament in the electron gun. In that case, a small 200 \( \ell / \text{s} \) turbo pump (Sargent Welch 3134) was used to maintain the vacuum at the cold finger. A butterfly valve was used to isolated the small turbo pump during normal operation. This convenient arrangement came about as a result of preliminary
work (Corr, 1987). It reduced the amount of exposure of the detector chamber to the atmosphere in order to maintain its cleanliness. A small window on the chamber permitted viewing of the xenon layer.

The two large turbo pumps were backed with a large rotary vane roughing pump (Edwards ED660). The detection chamber turbo pump was backed by a smaller rotary vane pump (Edwards ED100). Safety interlocks were installed to shut down the pumps in case of an interruption of the cooling water to the turbo pumps. The resulting vacuum was very clean and oil free, as evidenced by the minute trace of carbon deposits left on the electrodes of the electron gun. The oil free vacuum was necessary to avoid contamination of the cold finger, which is an effective cryopump for oil vapours.

The photomultiplier tube was set in a cradle attached to a liquid nitrogen reservoir and kept under a vacuum of about $10^{-6}$ torr by a two inch oil diffusion pump. The cold finger liquid nitrogen reservoir was evacuated to about 10 mtorr by a small rotary vane pump. A plexiglass shutter (S) attached to a rotary feedthrough could be used to block metastables from reaching the cold finger, but allow prompt photons through. This served as a diagnostic aid.

II. The Electron Gun and Gas Jet

The electron gun was a simplified version of the one described by Ajello et al. (1988). A scale diagram of the electron gun is shown in figure 4.2; the electrical
Figure 4.2  Cut away view of the electron gun, faraday cup, and gas jet. SR-support rods; FH-filament holder; EE-extraction electrode; CE-collimation electrode; CT-capillary tube; IC-inner cup; OC-outer cup; MR-magnetic rod. The positions of the magnetic rods are partially drawn in with a light dashed line. The inset shows the orientation of the magnet rods to the electrodes, and the slits to the gas jet. The heavy dashed line represents the magnitude of the magnetic field along the electron beam axis, according to the scale at right.

Figure 4.3  Wiring diagram for the electron gun operating in the pulsed mode. F-filament; EE-extraction electrode; CE-collimation electrode; OC-outer cup; IC-inner cup; FS-filament supply; FB-filament bias supply which determines the energy of electrons ($E_0$) along the axis at the interaction region.
connections are shown in figure 4.3. The design utilized a permanent magnet quadrupole to provide collimation of the electron beam. Electrons in the beam were kept from diverging due to the mutual electrostatic repulsion by the Lorentz force. All elements of the gun and Faraday cup system were machined from non-magnetic stainless steel with the exception of the molybdenum slit on the collimation electrode (CE). The slits measured approximately $1.0 \times 5.0$ mm. The filament was a thoriated iridium ribbon 0.75 mm wide. It typically required 5 to 6 amps of current to produce a usable beam.

Electrons were collected by a double faraday cup whose entrance was located 4.5 cm from the filament. The double cup design gave a rough measure of the beam divergence. All of the current (99.99%) entered the inner faraday cup (9.4 mm diameter by 11 mm long) which was biased with respect to ground. Currents measured by a digital ammeter (Keithley 480) were typically 1 mA d.c. in the absence of a gas jet. Figure 4.4 below shows a plot of beam current versus beam energy and illustrates the very good characteristics of the gun.

![Plot of current versus electron impact energy](image)

**Figure 4.4** A plot of current entering the inner Faraday cup versus electron impact energy using O₂ as the target gas (10 torr upstream of the nozzle). The inner Faraday cup was biased at +50 V, the outer cup at +10 V. Pulses were 20 μs long at a rate of 5.0 KHz.
The power supplies shown in figure 4.3 were stable, accurate, and precise units, manufactured by Lambda, Bertan, and Hewlett-Packard. During operation, the extraction electrode was biased -10 V with respect to the filament. Pulses of electrons (0.5 to 70 µs long) were obtained by applying a +35 V pulse to the extraction slit through the 0.1 µF capacitor. The 50 Ω resistor and 200 pF capacitor terminated the coaxial cable in order to reduce the reflection of high frequency components. Clean, square pulses with small overshoots were observed on a fast oscilloscope with a suitable probe. Beam currents were varied by adjusting the extraction pulse height. The digital ammeter had an integrating input, so it could be used to measure the pulsed currents entering the inner cup, with a relative accuracy of 0.5%.

The magnet quadrupole was made of four Alnico-V magnetic rods measuring 1.25 cm in diameter by 15 cm long with their axes 2.5 cm apart. The electrically grounded rods were clamped in their yokes with like poles at the same end. The magnetic field along the axis of the electron beam measured in situ (by removing the faraday cup) with a Bell 640 Gaussmeter is shown in figure 4.2 and was similar to that obtained by Ajello et al (1988). Further measurements off axis showed small deviations of about 5% at a distance of several millimeters. The precision was limited somewhat by the size of the Gaussmeter probe (5 mm diameter).

It was observed (through a window installed on the large chamber) during trial runs that the electron beam, made visible by admitting a small quantity of gas, was slightly curved by 1-2 mm. Optimization of beam alignment was then carried out by rotating the magnetic rods in their yokes to correct for small field assymmetries. This
was a tedious task since the rotations could not be carried out under vacuum. The result was a beam which appeared straight and uniform over its entire length and was well aligned as there was virtually no current incident on the outer faraday cup. It was not possible to view the beam from above the plane formed by the electron beam and line of sight to the detector. Thus, if there was a possible curvature which would affect the distance $D$ to the detector, it could not be assessed. The experience with rotating the magnets put an upper limit of about 2-3 mm on the uncertainty in $D$.

In addition to defining the beam shape and uniformity, another important consideration was the beam energy at the interaction region, $E_o$. $E_o$ was given by the voltage of the filament bias supply (FB). Since there was a $\sim$2 V drop across the portion of the filament which actually contributed to the collimated beam, $E_o$ represents the axial beam energy. The energy of the entire beam varies over its height. Some of this spread could have been eliminated by the use of an indirectly heated cathode, but the thoriated iridium ribbon is more resistive to the corrosive action of oxygen. Besides the spread in beam energy brought on by the voltage drop across the filament, thermionic emission results in a Maxwellian type distribution of electron energies leaving the surface. This spread is typically about 2 eV for a filament at 2320 K (Field and Franklin, 1970).

There were several other factors to consider as well. Contact potentials arise from the dissimilar metals used in the electric circuit (Melissinos, 1966). They can also change as the work function of the filament surface can be affected chemically.
by exposure to different gases from the interaction region (Field and Franklin, 1970). Contact potentials typically have a magnitude from 0 to 2 V.

The mutual electrostatic repulsion of electrons in the beam (space charge) leads to a depression of the potential at the interaction region. It was observed that thresholds (e.g. see chapter 6) could be shifted several volts by using too high a beam current. One further influence on the energy of the electron beam was the voltage applied to the inner Faraday cup. There was significant field penetration extending into the interaction region which could also change the average beam energy by several volts when the inner cup was at +50V. Field penetration also increases the spread in energies over the collision volume defined by the intersection of the gas jet and electron beams, but this effect was insignificant at the energy resolution available. Beam energy calibration for threshold studies is described in chapter 6. It was carried out in such a way that it automatically accounted for all of the effects.

The axis of the capillary tube (CT) was located 2.5 cm from the filament of the electron gun, with its orifice about 7.5 mm from the axis of the electron beam. The orientation of the gas flow with respect to the electron beam is shown in the inset of figure 4.2. The capillary tube was made from demagnetized stainless steel 2.3 cm in length with an internal diameter of 0.66 mm. An MKS Baratron gauge (BG) was used to measure source pressure upstream of the needle, $P$. At a typical operating pressure of $P \approx 10$ torr, the background pressure in the large chamber was of the order $10^{-4}$ torr. The purity of all gases used in this work was 99.99% or better, according to the manufacturer (Matheson or Linde).
III. The Detector

The cold finger (CF) on which the xenon layer was grown was made from a solid copper rod 2.5 cm in diameter, which was in contact with a liquid nitrogen reservoir. Its tip was polished to a mirror finish and the entire rod was nickel plated. All parts of the rod exposed to the vacuum were covered with a 2.5 mm thick teflon sleeve, except the surface on which xenon was deposited. This acted as a conservation measure since xenon readily condenses on the nickel plating, but not on the teflon.

A copper-constantan thermocouple fixed near the tip was used to measure temperature. A small wire gauge was used to reduce heat conduction from the cold finger. The thermocouple wires were passed unbroken through two electrical feedthroughs sealed with solder. Outside the vacuum they were soldered to copper wires to form a reference junction. The junction was placed in an insulating bottle at room temperature along with an accurate precision thermometer. By measuring the temperature of the junction, and using a sensitive digital voltmeter (Fluke 8350A) to measure the resulting EMF, the cold finger temperature was calculated. For this purpose, a program was written to do a fourth order polynomial interpolation of the National Institute of Standards and Technology (US) 1990 thermocouple data. Calibration with liquid nitrogen (boiling point = 77.4 K at atmospheric pressure) ensured the accuracy. With a full cryostat, the cold finger temperature reached 84.9 K at equilibrium. The difference was attributed to heat absorbed by the cold
finger from the blackbody radiation of its surroundings, and heat conduction to the cold finger by the supports and rough insulating vacuum.

By reducing the vapour pressure of LN₂ to about 100 torr (measured by a Bourdon gauge) with a mechanical pump, its temperature reaches 63.5 K, resulting in a cold finger temperature of about 71K. At this temperature the xenon vapour pressure is about $4 \times 10^{-4}$ torr (see figure 4.5(a)). This is low enough to allow the O(^1S) atoms from the main chamber to reach the cold finger without significant attenuation. Figure 4.5(b) shows a plot of LN₂ vapour pressure versus temperature.

![Figure 4.5](image)

(a) Sublimation pressure of solid xenon versus temperature. The data above 71 K is from direct measurement (Leming and Pollack, 1970), while the data below was generated by a seventh order polynomial extrapolation (Corr, 1987).

(b) Vapour pressure of liquid nitrogen versus temperature based on the data from White (1968) and a seventh order polynomial interpolation (Corr, 1987).
The pumping of the LN$_2$ was regulated manually with a throttling valve. Once the cryostat was filled (15 $\ell$ capacity), the throttle to the rotary vane pump (Edwards ES 150) was then set fully open for 40-50 minutes to quickly reduce the cold finger temperature to 71 K. The throttle was then partially closed to reduce the cooling of the LN$_2$. If it was left fully open the LN$_2$ would solidify. After the throttle was set, the cold finger would warm up slightly to 74 or 75 K, and then gradually fall over the next 24 hours as the LN$_2$ volume decreases. Eventually the throttle setting results in too great a pumping speed for the small volume of LN$_2$ remaining and it freezes (at 63.15 K). Unless there was intervention from the operator, the cold finger would warm up rapidly due to the poor thermal conductivity of the solid nitrogen.

During operation the butterfly valve to the 200 $\ell$/s turbo pump was closed. Xenon was admitted into the cold finger chamber by a needle valve. A Granville-Phillips Convectron gauge (CG in figure 4.1) placed just down stream of the needle valve was used to monitor the xenon pressure at that point.

Metastable O($^1S$) atoms reaching the solid xenon quickly form excimer complexes which rapidly fluoresce. The photons produced were detected by a cooled Hamamatsu R943-02 Ga-As photo-multiplier tube (PMT). The PMT was in a magnetically shielded cradle lined with teflon. The cradle was in good thermal contact with a reservoir of liquid nitrogen. The entire assembly was under a high vacuum ($10^{-6}$ torr) created by a 2 inch oil diffusion pump. The teflon liner was necessary to insulate the glass tube from the metal cradle. Otherwise, during cooling,
thermal stresses develop in the glass from direct contact with the metal and these could result in cracking.

The dynode chain of resistors for the tube followed the manufacturer's recommendations. The network was wired on a fiberglass circuit board, and was in the vacuum with the PMT. Each pin from the PMT was wired individually (not soldered) to the dynode chain. Using a socket for such low temperatures could place thermal strain on the pins when cooled and could crack the tube. Three hours were required to cool the tube from room temperature to about 77 K. Cooling took place predominantly by radiative transfer from the tube to the cradle. Dark counts were about 3 per second at 77 K. The cathode of the PMT was located 23.6 cm away from the xenon surface. Its quantum efficiency as a function a wavelength is plotted in figure 4.6. Pulses from the photomultiplier were typical of a PMT with a linear focused dynode arrangement, having a width of several nanoseconds and very little ringing. The PMT was operated at a bias of 1800V.

Provision existed for the placement of either filters or a monochromator between the cold finger and the photomultiplier. Transmission curves for the filters used are shown in figure 4.7. The monochromator was a PTR Optics Model MC1-03 F/4 Fastie-Ebert Mini-Monochromator with a range of 300-850 nm and a linear dispersion of 6 nm per mm. No attempt to measure its transmission versus wavelength was made. The monochromator was housed in a light tight box. Light entering the box was focused by a 2 cm diameter quartz lens onto the entrance slit of the monochromator. It emerged from the exit slit and travelled through a second
Figure 4.6  Quantum efficiency of the gallium-arsenide photocathode of the Hamamatsu R943-02 photomultiplier tube, from the manufacturer.

Figure 4.7  Transmission curves for the various filters used in this experiment as measured with a spectrophotometer. The filters are identified by their catalogue number (Corion).
identical lens before leaving the box. Both lenses were fixed so that the slits were at their focal points. A long wave pass filter which transmitted above 450 nm could be flipped into position when working above those wavelengths. This eliminated 2nd order images. The transmission range of the BK-7 glass windows between the Xe layer and the photomultiplier went from 260 nm to the infrared.

IV. Data Acquisition

a) Pulse Handling Electronics

Pulses from the photomultiplier were processed by standard nuclear instrumentation modules (NIM). Refer to figure 4.1 for the layout. An Ortec 9301D fast pre-amplifier (PRE) with a gain of 10 was connected to the photomultiplier output. These pulses entered a fast pulse amplifier (A, Ortec 474) which was set at a gain of 250. The fast amplifier had pulse shaping capabilities but these were not used. Pulses with an average height of 1 to 2.5 volts left the fast amplifier and entered a fast pulse discriminator (D). In this case a timing single channel analyzer was used (Ortec 551).

The timing single channel analyzer could be used to acquire a pulse height distribution from the amplifier output in order to determine the optimum discrimination level. Referring to figure 4.8, 0.50 volts was chosen to eliminate the photomultiplier dark counts and noise responsible for the sharp increase in pulses
with heights below $\frac{1}{2}$ V. Sources of noise included pick up from the electron beam pulser and computer monitors.

![Pulse height distribution from fast amplifier output for the photomultiplier exposed to very weak illumination.](image)

Fast risetime pulses from the discriminator were fed into the stop input of a time-to-amplitude convertor (TAC, Ortec 467). The start input was connected to the master clock (MC). The master clock was a homemade unit with four digitally delayed outputs. One of these outputs went to the TAC start, and the other to the electron gun pulser (P). The pulser was also a homebuilt unit capable of delivering 0.5 to 70 $\mu$s wide pulses with amplitudes from 0 to 35 volts with a 200 ns risetime and 50 ns falltime into a high impedance load.

The TAC produced a 3 $\mu$s wide pulse whose height (0-10V) was directly proportional to the time interval between the start and stop pulses. A front panel knob sets the conversion factor but the unit had to be calibrated. The TAC also has a second output which produced a TTL logic pulse if the 0-10V timing pulse had an
amplitude which was between a lower and upper level threshold. This feature was used to set a gate over certain time intervals in time-of-flight spectra for accumulation of excitation functions.

The TAC output was fed to the input of a pulse height analyzer (PHA, Nucleus PCA-II). That unit was built on a circuit board which fitted into an expansion slot of an IBM AT personal computer. The PHA quickly converted pulse amplitudes from the TAC to either an 8, 9, or 10 bit number and incremented the counter (or channel) with that address by one. The screen displays the contents of all 256, 512, or 1024 channels.

b) Acquiring Time-of-Flight Spectra

Time-of-flight (TOF) spectra were acquired by preparing the xenon surface, setting the electron gun in pulsed mode, introducing the sample of gas to be studied and letting the PHA run until time had elapsed for sufficient statistics. At each pulse of the electron gun, the TAC was started, then stopped by the detection of a photon, produced an output for the PHA, and reset itself, ready to be triggered by the next shot of electrons. The shot rate ran from 1.0 to 5.0 KHz. TOF spectra were saved to a floppy disk for further analysis. Figure 4.9 shows a typical TOF spectrum.

Usually, the electron gun pulse was delayed by several microseconds after the TAC had been started to include the prompt photons in the TOF spectra. These prompt photons were produced when the electron beam was on, and come from
electron impact excitation of the target gas molecules in the collision region. They were scattered into the photomultiplier tube off of the xenon surface. The prompt photons serve as the zero mark on the time scale in TOF spectra.

![Graph showing time-of-flight spectrum with counts per channel and time-of-flight (µs) axes. Channel width = 0.57 µs.]

**Figure 4.10** Example of a time-of-flight spectrum from 100 eV electron impact on N₂O. Electron pulses were 1 µs long. The high count in the early channels comes from the prompt photons emitted while the electron beam was on and the structure at 52 µs comes from the arrival of O(^1S) atoms at the surface of the xenon. See chapter 6.

Calibration of the time scale was done by using the master clock. A pulse from the clock was fed to the start input of the TAC, and a digitally delayed pulse was fed to the stop input. A pulse height spectrum was acquired while incrementing the delay in 5.0 or 10.0 µs steps. The result was a conversion factor which was the width in µs for each channel in the pulse height analyzer. Because channels are discrete, the calibration was limited in precision to the width of the channel.
Since the TAC can only produce one timing pulse for every shot, ignoring photons which arrive after it has received the first stop pulse after the start, it was possible for the prompt photons to stop the TAC every time it was triggered. This dead time was avoided by working with count rates of less than one per shot.

While acquiring TOF spectra over long ranges (800 µs), the background in the spectra from photon events which were uncorrelated with the electron pulses (stray light from the electron gun filament, dark counts, cosmic rays) tended to have a slight negative slope to it. This was also due to TAC dead time and can be understood as follows.

Suppose there is no target gas. Then the only TAC stops possible come from the uncorrelated photons. If these photons arrive at the detector at an average rate \( \alpha \) counts per second, and since their arrival can be described by a Poisson process, then the probability distribution function \( p(t) \) that describes the time \( t \) that the TAC will be stopped is

\[
p(t) = \alpha e^{-\alpha t}.
\]  

(4.1)

The probability that the \( k^{th} \) channel in the TOF spectrum will record a count is then

\[
\alpha \int_{k\Delta t}^{(k+1)\Delta t} e^{-\alpha t} dt = e^{-\alpha k\Delta t} [1 - e^{-\alpha \Delta t}]
\]  

(4.2)

where \( \Delta t \) is the channel width. The background has the shape of a falling exponential. If the background count is very low (as it usually is), then the background is a
straight line with a negative slope. This is easy to show by expanding the exponential in a Taylor series and omitting the higher order terms.

c) Acquiring Excitation Functions

The Nucleus Model PCA-II pulse height analyzer card also had a built in multi-channel scaler (MCS). To acquire an excitation curve, the TAC start was delayed until the impending arrival of metastable particles at the detector. The TAC was set up to cover the spread of arrival times of the metastables by a suitable adjustment of its range. This amounted to setting up a window in the TOF spectrum which was delayed to collect only the photons arriving in the time range of interest. The TTL logic output from the TAC was fed to the input of the MCS.

As the MCS advances through its channels it produces a voltage proportional to the current channel number (to 5 V max). This was used to control the output of an analog programmable d.c. power supply for the cathode bias, E\text{c}. In this way the yield of metastables as a function of electron impact energy was accumulated as the MCS was repeatedly swept over the range of channels. Low count rates were used to ensure a negligible TAC dead time effect.
d) Linearity Checks

A measurement of the metastable count rate versus electron beam current ($I$) and source pressure ($P$) was necessary to demonstrate that production takes place from single collisions. The high count rates which occur for these checks could not be measured using TAC gating as described above. Instead, a counter gated by a suitably delayed pulse from the master clock was used. Throughout these linearity checks, the count rates were still low enough for single photon counting, i.e. the fraction of two photon arrivals at the photocathode was negligibly small. The results of these tests will be presented for the different target gases in the following chapters along with TOF spectra and excitation functions, following a description of the operation of the xenon layer metastable detector.
Chapter 5

The Xenon Layer Metastable Detector

I. Historical Background

As mentioned in the introduction, studies of $O(^1S)$ in the laboratory are made difficult by its long lifetime. That was why identification of the $O(^1S-^1D)$ auroral line at 557.7 nm was not possible until the work of McLennan and Shrum (1926) who were the first to observe and identify it in a laboratory. The $O(^1S)$ state was excited by electrical discharge in a tube containing 30 torr of He with a trace of $O_2$. Although not understood at the time, they were able to observe the forbidden transition because the He atoms slowed the diffusion of the $O(^1S)$ atoms to the walls of the apparatus by elastic collisions, keeping the $O(^1S)$ atoms in the field of view of the spectrometer. This method is known as buffering and is still in use for
observation of the spectra, and the production and extinction mechanisms of metastable species. See for example Taherian and Slanger (1985) who made a study of the products and yields following photodissociation of \( \text{O}_3 \) in a helium buffer.

Spectroscopists turned to other rare gas buffers as they became available. Herman (1946) and Kenty et al. (1946), observed a remarkable modification to the 557.7 nm line when Xe was used as a buffer in an experiment similar to McLennan and Shrum. The line was replaced by an extremely intense band in the same region that could only come from vibrational transitions in a diatomic molecule. It was correctly concluded (Herman & Herman, 1950) that the \( \text{O}^1\text{S} \) atoms produced in the discharge had formed a weakly bound molecule with Xe in an excited energy state designated \( \text{XeO}^* \). Such molecules which are bound only at excited energy levels, and are not bound in their ground state, are called excimers. The green bands corresponded to transitions between \( \text{XeO}^1\text{S} \) and \( \text{XeO}^1\text{D} \), and their intensity demonstrated an effective shortening of the \( \text{O}^1\text{S} \) lifetime by at least a factor of \( 10^5 \). Herman and Herman (1950) also observed a weaker continuum band in the U.V. peaked at 308 nm which came from \( \text{XeO}^1\text{S} \) to \( \text{XeO}^3\text{P} \) transitions. No features corresponding to an \( \text{XeO}^1\text{D} \) to \( \text{XeO}^3\text{P} \) transition were observed.

Further spectroscopic work by others, such as Cooper et al. (1961) and Simmons et al. (1979) has led to the identification of the low lying excimer states of \( \text{XeO}^* \) and to a partial construction of the potential energy curves for each of those states. The \( \text{XeO}^1\text{S} \) excimer was even made to lase (Powell et al., 1974). Dunning and Hay (1977) have calculated \textit{ab initio} potential curves for the covalent states of
XeO in its gas phase, figure 5.6. These curves are only in qualitative agreement with experiment as they have no potential minimum for either the XeO(2^1\Sigma^+) and the XeO(1^1\Pi) curves. These states do have minima, which Simmons et al. (1979) have determined to be at 2.852 and 2.548 \text{ Å} with a depth of 0.086 and 0.057 eV respectively, and are also shown in figure 5.6. The deep well for the XeO(1^1\Sigma^+) state has not been determined from experiment because of the severe pre-dissociation in the 2^1\Sigma^+ \rightarrow 1^1\Sigma^+ transition. The data that has been gathered is consistent with Dunning and Hay's calculation of a 0.7 eV well depth for the 1^1\Sigma^+ state.

Studies of the emissions from rare gas solids containing small amounts of impurities, a field known as matrix isolation spectroscopy, date back to the 1920's. Vegard (1924) may have observed the O(1^3S \rightarrow 1^3\Pi) 557.7 nm transition in solid N_2:Ar mixtures bombarded by electrons. It was realized later that the green line emission may have been due a small amount of oxygen impurity in the N_2:Ar mixture (Vegard and Kvit, 1948).

Schoen and Broida (1960) obtained spectra from high energy electron bombardment of rare gas solids containing 1% O_2. The results show that the 557.7 nm auroral line is increasingly red shifted and broadened on the red side as one progresses from Ar to Xe. Of particular interest to this present work was the appearance of emission bands at about 370 nm and 550 to 750 nm in Xe, similar to the features in figure 5.5. Vibrational structures were not observed.

Further results were recently acquired by Yurtaeva et al. (1995), who repeated the work by Schoen and Broida and extended the spectral range into the V.U.V. In
the visible region, they obtained results similar to Schoen and Broida. They observed increased broadening and red shifting of the O(1S - 1D) and the O(1D - 3P) transitions in the order Ne, Ar, Kr. In Xe they also observed a band peaked at 373 nm, a broad weaker band in the green around 570 nm, and a much brighter band at 720 nm. Again, vibrational structures were not observed.

An accurate measurement of the lifetime for the XeO(2^1Σ^+) state in a matrix was obtained by Goodman et al. (1977). They studied the time, wavelength and polarization resolved fluorescence of XeO\(^+\) in an Ar matrix following excitation by pulsed U.V. laser light at 220 nm. This technique was used to fix XeO\(^+\) molecules for study in a medium that allows them to behave as if in a gaseous state. Indeed, they obtained beautiful spectra of the green bands which arise from the 2^1Σ^+ - 1^1Σ^+ transition. These were nearly identical to the gas phase spectra without the rotational development. In addition, they were able to show that the well depth of the 1^1Σ^+ state is unambiguously deeper in solid argon than in the free gas phase, and they observed transitions from a charge transfer Xe\(^+\)O\(^-\) state that is higher than the 2^1Σ^+ by about 0.75 eV, which were not seen in gas phase experiments. They measured a lifetime for the XeO(2^1Σ^+) state in Ar of 112 ns at 22 K.

It was this dramatic shortening of the O(1S) lifetime by Xe that gave Kiefl et al. (1983) the idea to use frozen Xe as a means to detect O(1S) atoms. Since the lifetime of O(1S) atoms in a Xe matrix would be small compared to their time-of-flight, they built an apparatus similar to the one described in this report to obtain accurate time-of-flight spectra of O(1S) atoms following electron impact dissociative
excitation of O$_2$. They observed green emissions from the Xe surface that was bombarded with O($^1$S), in agreement with the gas phase emissions already described. They used their apparatus to obtain extinction cross sections for O($^1$S) and various gases but abruptly ceased work on the novel detector citing a change of emphasis in research goals (Fricke, 1987).

A second attempt at using this type of detection scheme is described in the work of Corr (1987). It was only partially successful. There were problems with the electron gun surviving in the corrosive O$_2$ atmosphere, and beam currents were too low to produce a usable O($^1$S) signal. O$^+$ ions were observed in TOF spectra as they produced a bright fluorescence signal when impinging on the Xe layer.

In what follows, the preparation and functioning of the Xe layer detector used for the research of this thesis will be described.

II. Preparation of the Solid Xenon Surface

Once the cold finger reached 71 K, a Xe layer was formed by flooding the detector chamber with Xe to a pressure of about 10.0 mtorr for one minute. The Xe pressure was then reduced to just above the pressure required to maintain a continuously condensing surface (from figure 4.5). This produced on the cold finger a thin, matt white, opaque layer of Xe which resembled fine white paper. Solid Xe is transparent, with a face center cubic structure having a lattice constant of 6.18 Å at 70 K (Pollack, 1964). The appearance of the layer was indicative of a
polycrystalline grain size less than a tenth of the wavelength of violet light (4000 Å) for it to have scattered incident white light without any discoloration. The reason for flooding the chamber was simply to establish an opaque covering on the highly reflective cold finger surface as quickly as possible in order to begin the experiment. Otherwise the high prompt photon count rate would result in too many premature TAC stops and the dead time would prevent the observation of metastables arriving at the Xe surface.

III. Factors Affecting Detector Performance

The 10 mtorr absolute pressure was measured during the rapid deposition with a Baratron gauge temporarily installed on the cold finger chamber. At that pressure, the convectron gauge (CG in figure 4.1) measured 1.0 torr, but it was uncalibrated for Xe. The convectron gauge was used to simply monitor the Xe. When the Xe pressure was reduced to the normal operating point the convectron gauge measured about 60 mtorr.

The normal operating point for the Xe pressure was established empirically by measuring the yield of O(^1S) from N₂O versus convectron gauge pressure. The results are shown in figure 5.1. It is clear from the diagram that there was still a usable signal even after the Xe flow was cut off from the layer.

Initially, this was thought to be advantageous since maintaining a steady flow of Xe was costly. However, after 20 hours the metastable signal fell to 10% of the
intensity with a continuous flow. This was probably due to increasing concentrations of condensable impurities on the Xe surface, such as the target gas itself. In the earlier stages of the experiment the cold finger would collect enough oil to form tiny droplets. The appearance of oil seriously degraded the detection efficiency. It was cleaned with alcohol. Further work demonstrated that the oil came from the small 200 ε/s turbo pump on the cold finger. The problem was eliminated by reducing the oil filling charge. At the time of writing the problem has not reappeared.

![Graph](image)

**Figure 5.1** Yield of O(\(^3\)S) atoms versus Xe pressure as measured with the convectron gauge.

It was decided that a continuous flow of Xe was required to maintain a fresh surface, usually at 60 mtorr. It is also evident from figure 5.1 that if there was too much flow then the count rate dropped as the metastable atoms were attenuated.
before reaching the cold finger. This probably took place either by elastic scattering 
or collisional quenching.

A further example of the necessity for continuously refreshing the Xe surface 
is illustrated by figure 5.2. Here a thick Xe layer was prepared and N$_2$O was used as the target gas for O(1S) production. Then the Xe flow was stopped and the butterfly valve to the turbo pump opened. As is clear from figure 5.2 the sensitivity of the surface dropped rapidly over several minutes. Restoration of sensitivity was equally rapid when the valve was closed and the pressure in the chamber reverted to some equilibrium pressure governed by the vapour pressure of Xe at the temperature of the cold finger.

Figure 5.2  Variation of detector sensitivity as a function of time using N$_2$O as the target gas. The sharp discontinuities at 4 and 34 minutes occurred with the opening and closing, respectively, of the valve between the detector chamber and the turbo pump. The rise in the count rate at 67 minutes occurred when Xe flow was recommenced.

Once the Xe flow was recommenced, the count rate increased by a further 20%. When O$_2$ was used as the target gas the contamination of the Xe surface was
much slower when the valve flow was opened and the recovery of sensitivity was also much slower when the valve was closed. This probably indicates that the dominant source of contamination in the case of N$_2$O was the N$_2$O itself which readily sublimates at 70 K. O$_2$ does not condense at 70 K unless its pressure is about 50 torr. Hence for O$_2$, the dominant source of contamination would come from other impurities in the vacuum system. Support for this mechanism of contamination came from calibrated (Bartness and Georgiades, 1983) ion gauge measurements of the background pressure of those two gases in the detector chamber while the cold finger was at 70 K. Using identical source pressures of 10 torr, the pressure of N$_2$O and O$_2$ in the cold finger chamber was $1.5 \times 10^{-6}$ and $4.5 \times 10^{-5}$ torr respectively. It was also observed that a solid N$_2$O surface did not produce any detectable signal.

The behaviour and sensitivity of the Xe surface detector was found to depend on a number of other factors which were investigated as discussed below. The most significant factor was the temperature of the Xe surface. Figure 5.3 shows a plot of how the sensitivity varies with temperature illustrating that a change in temperature of even 1K can have a significant effect on the observed count rate. Some of the apparent drop-off in sensitivity with increase in temperature may be caused by enhanced collisional quenching of the metastables by the higher Xe vapour pressure.

When continuous deposition of Xe was occurring, the Xe layer eventually became thick enough (several mm) that a considerable thermal gradient existed between the exposed surface and the underlying copper finger. This resulted in a drop in sensitivity. For this reason the detector was not operated continuously for
longer than one week. At the end of this period the Xe was allowed to evaporate from the finger and then a fresh surface was formed.

![Graph showing the variation of metastable count rate as a function of cold finger temperature.](image)

**Figure 5.3** Variation of metastable count rate as a function of cold finger temperature. N₂O was used as the target for O(1S) production. O₂ produced identical results.

Occasionally, flashes of light originated from the solid Xe. Others have reported similar effects (Yurtaeva et al., 1990). In this case, they usually appeared when the layer had grown quite thick. It was thought that the flashes originated from
internal stress due the thermal gradient across the layer. Cracks might suddenly form as a result of the stress, accompanied by a flash of light. This would be a manifestation of the phenomenon known as triboluminescence (Angelos et al., 1979; Dickinson et al., 1991). The bursts of light were easily captured on the multichannel scalar using a 1 ms dwell time, and one is shown in figure 5.4.

![Diagram](image)

**Figure 5.4** Flash of light emitted by the Xe layer captured on the multichannel scalar with a 1 millisecond dwell time. The solid line is a double exponential fit by eye.

Time did not permit a detailed study of the flashes. The one captured in figure 5.4 is a representative sample. It has a quick rise to maximum intensity (≈1 ms) followed by a decay that was best fit by eye by two exponentials with lifetimes of 10 and 55 milliseconds. These flashes have only been observed when working with $\text{N}_2\text{O}$ as the target gas. Once started, they seemed to continue indefinitely, and the only way to remedy the situation was by removing the Xe layer.
and growing a new one. The flashes were observed regardless of which filters were used on the photomultiplier, so they cover a broad spectral range.

These brief flashes were clearly visible to the naked eye. They were much brighter if a layer of Xe was grown over a layer of N₂O and the liquid nitrogen was allowed to run out to cause a rapid rise in the cold finger temperature. The spectacular display had the appearance of a tiny flashes of diffuse chain lightning within the layer. It was also possible that the effect was thermoluminescent (McKeever, 1986). In that case heating of the layer releases electrons trapped at defects in the crystal. These higher lying electron states could have been populated by the bombardment of the layer by U.V. radiation from the excitation of target gases in the interaction region.

IV. Spectra of XeO⁺ Emissions and Mechanism of Light Production

The spectral distribution of light emitted from the Xe surface, when N₂O and O₂ are the target gases, is shown in Figure 5.5 (a) and (b) respectively. The spectra were obtained by acquiring TOF spectra from the two gases while advancing the monochromator in 25 nm intervals. Since the count rates were low, the electron pulses used were 20 µs long, and no slits were in place on the monochromator resulting in a bandpass of about 20 nm. Each TOF spectrum was gathered in 15 minutes. The amount of XeO⁺ emission was extracted from each TOF spectrum by taking the difference between the total count in the channels spanning the arrival
Figure 5.5 Low resolution optical spectra of XeO⁺ emissions from the xenon layer using N₂O (a) and O₂ (b) as the target gases. Note the factor of 5 magnification applied to the data from N₂O below 600 nm. Error bars are placed on the data from O₂ only because of the low counts. In both cases a smooth curve was drawn through the data to guide the eye.
times of the O(1S) metastables (50 to 70 µs for N₂O and 35 to 55 µs for O₂) and the
total count in a similar span of channels well after all of the metastables have arrived
(background).

The low resolution curves, which have not been corrected for the variation
with wavelength of the sensitivity of the monochromator-PMT detection system, show
features at 375 and 725 nm. With N₂O as the target gas an additional faint green
emission at 550 nm can be seen. That particular feature is not present in the
spectrum with O₂ as the target gas probably because it produces much less O(1S)
than N₂O following electron impact dissociation. See the results of chapters 6 and 7.
The three emission features observed from the N₂O target are very similar to the
features observed in the spectra of Yurtaeva et al. (1990) and Schoen and Broida
(1960) mentioned in section I of this chapter.

It is noted that Kiefl et al. (1983) reported only green emission from their
surface using a similar arrangement with O₂ targets. They did not observe the U.V.
or red-infrared emissions which dominate the spectrum in the present results. Their
photomultiplier was sensitive from 200 to 600 nm, which accounts for overlooking the
red emission. This can only suggest that remaining difference is due either to the fact
that their cold finger may have been at a different temperature, or that they grew
their Xe layer differently (Kiefl, 1983), or both.

Monahan and Rehn (1978) have observed a strong I.R. emission following
photolysis of N₂O in solid Xe by V.U.V. radiation, and concluded on energetic
grounds that it was due to a red shifted O(1D) - O(3P) transition in the Xe matrix.
Applying this to the present results would suggest that most of the \( O(^1S) \) atoms impinging on the \( \text{Xe} \) surface undergo a radiationless transition to the \( \text{XeO}(^1\text{D}) \) state, while others did radiate at 375 nm to the same state. This would be followed by the red transition from \( \text{XeO}(^1\text{D}) \) to \( \text{XeO}(^3\text{P}) \).

This has three difficulties. Firstly, a 375 nm photon decay followed by a 725 nm decay to the ground state would mean that the \( \text{XeO}(^1\text{S}) \) excited state should be more than 5.0 eV above the ground state which is hardly feasible. Secondly, it contradicts theory (Maillard et al. 1983) which predicts a non-radiative transition of \( O(^1\text{D}) \) to the ground state in a \( \text{Xe} \) matrix. Thirdly, \( O_2 \) produces copious \( O(^1\text{D}) \) following electron impact (Stone et al., 1975) and the results in chapter 7 demonstrate the insensitivity of the \( \text{Xe} \) layer to that species.

A better explanation of the \( \text{XeO}^+ \) spectra is based on the timely work of Lawrence and Apkarian (1992).

They have observed an emission spectrum identical to those in figure 5.5 (except for the faint green emission) following intense laser U.V. irradiation of solid \( \text{Xe}:\text{N}_2\text{O} \) mixtures. Briefly, they explained their result as follows. Atomic oxygen dissociated from \( \text{N}_2\text{O} \) would find itself inserted at an interstitial site of octahedral symmetry in the solid \( \text{Xe} \). From there, it was excited to the ionic \( \text{Xe}^+\text{O}^-(3^3\Sigma^+) \) state about 5 eV above ground which relaxed to its potential minimum at about 4 eV. This minimum is shown in figure 5.6, and lies below the potential curve for the covalent \( \text{XeO}(2^1\Sigma^+) \) state and, as a result, there is an avoided curve crossing. The ionic state would then undergo a radiative transition to the repulsive wall of the
Figure 5.6 Xe\(^{(1)S}\)–O potential curves with the transitions observed in figure 5.5. The dashed curves are taken from Dunning and Hay (1977) and Simmons et al. (1979) while the solid curves are from Lawrence and Apkarian (1992).
XeO(\textsuperscript{1}\Pi) state, producing the near I.R. emission, or to the potential minimum of the XeO(\textsuperscript{1}\Sigma+) state at 0.6 eV to produce the near U.V. emission. Either way the Xe + O(\textsuperscript{1}D) states that would be created undergo non radiative transitions to the ground state.

The dashed lines in figure 5.6 are the accurate \textit{ab initio} potential curves of Dunning and Hay (1977) for the lowest covalent states of XeO in the gas phase, except the \textsuperscript{2}\Sigma\textsuperscript{+} and \textsuperscript{1}\Pi states which come from the experimental results of Simmons et al. (1979). The ionic state Xe\textsuperscript{+}O\textsuperscript{-}(\textsuperscript{3}\Sigma\textsuperscript{+}) has never been observed in the gas phase, but according to Lawrence and Apkarian, its existence was inferred because Xe\textsuperscript{+}O\textsuperscript{-} is isoelectronic with IF, and such states have been reported in rare gas matrices before, as in the work of Goodman et al. (1977) mentioned in section I. Lawrence and Apkarian calculated its gas phase minimum to lie at about 2.3 Å, at an energy 4.6 eV, therefore overlapping with the repulsive wall of the covalent XeO(\textsuperscript{2}\Sigma\textsuperscript{+}) state. In the solid phase, the gas phase minima of the Xe\textsuperscript{+}O\textsuperscript{-}(\textsuperscript{3}\Sigma\textsuperscript{+}) and XeO(\textsuperscript{1}\Sigma\textsuperscript{+}) states are lowered to the positions indicated in figure 5.6. This is not at all unreasonable since Goodman et al. (1977) observed a deepening of the potential minimum in the \textsuperscript{1}\Sigma\textsuperscript{+} state in an argon matrix. In view of their experimental work, detailed analysis, and modelling of the transitions, it is concluded that the light production from the Xe detector described in this paper proceeds along the same lines, only the upper state is populated by the O(\textsuperscript{4}\S) atoms inserted into the matrix following the termination of their flight path.
Note that the gas phase Xe-O potential curves in figure 5.6 serve as qualitative representations of the energy levels of O atoms in solid Xe. A more accurate picture of the interaction energy of an oxygen atom in a xenon matrix is found in the work of Mallaird et al. (1983).

The faint green emission observed when N₂O was used as the electron impact target to give a more intense source of O(¹S) has not been reported by Lawrence and Apkarian (1992), nor by others (Monahan and Rehn, 1978; Kruger and Weitz, 1992) irradiating Xe:N₂O mixtures, nor was it predicted by theory (Maillard et al., 1983). It is possible that this is a gas phase XeO(2¹Σ⁺ -1Π) transition which could take place if, in the process of thermalization, a slow O(¹S) atom were to form a n excimer with the condensing Xe gas, i.e., the green emission is a surface phenomenon. Such a feature would not be seen in the aforementioned experiments because they operated at lower temperatures (25 K) and background gas pressures than the present detector.

The conversion time of the detector has not been measured but, based on the fragment kinetic energy data presented in the succeeding chapters and on comparison with spectroscopic information regarding the known positions of repulsive potential energy curves, for example in N₂O, it cannot be more than few microseconds. This is the time taken for the O(¹S) atoms to thermalize and come to an equilibrium position within the Xe matrix. Once in position, the life time of the upper state can be estimated from the work of Lawrence and Apkarian (1992) to be about 100 ns.
An approximate estimate of the quantum efficiency $q$ of the detector was obtained from the $\text{N}_2\text{O}$ measurements. It was possible to put these measurements on an absolute basis as discussed in the chapter 3. Knowing the absolute cross-section for production of $\text{O}^1\text{S}$ from electron impact on $\text{N}_2\text{O}$ (chapter 6), together with measurements or estimates of the electron beam current, the target gas density, the solid angle subtended by the detector, and the attenuation of $\text{O}^1\text{S}$ en route to the detector (Kiefl et al., 1983) allowed an estimate of the number of $\text{O}^1\text{S}$ atoms produced in the collision which would reach the detector surface (equation 3.18). An estimate also could be made of the total number of resultant photons from the detector which were recorded by the photomultiplier. This comes from a knowledge of the various optical transmission factors, the quantum efficiency of the photomultiplier, and the solid angle subtended by the photomultiplier. The ratio of these two numbers gave the quantum efficiency of the detector directly. The value obtained was $q=0.25$. The greatest uncertainty in this procedure came from the estimation of the target gas density since this was based on measurements of the source pressure (using a Baratron) together with calculated flow rates (Lucas, 1973). Other uncertainties arose in the estimation of the beam overlap geometry and of the $\text{O}^1\text{S}$ quenching en route to the detector surface. Both the $\text{O}^1\text{S}$ production process and the photon emission process from the detector surface were assumed to be isotropic. In all cases, conservative estimates were made so that the figure quoted represents a lower limit to the actual quantum efficiency.
Chapter 6

The Results Obtained from Nitrous Oxide

I. Review of Earlier Work

$\text{N}_2\text{O}$ has been studied often because of its importance as an anaesthetic and the role it plays in the stratosphere. In particular, it is a source of NO which contributes to the destruction of ozone (Rees, 1989). It is a linear molecule having the structure $\text{N}−\text{N}−\text{O}$ with $\text{N}−\text{N}$ and $\text{N}−\text{O}$ bond lengths of 1.128 and 1.184 Å respectively. Its ionization potential is 12.894 eV (Herzberg, 1967). Many of the electronic states of this molecule have been calculated by Hopper (1984). The linear molecular states are represented in figure 6.1 on the following page. Each molecular state is joined by a line which represents the adiabatic connection to the asymptotic states of N and NO or $\text{N}_2$ and O which they correlate to.
Figure 6.1  Adiabatic correlation diagram of the linear states for the nitrous oxide system (N – NO, N₂O, N₂ – O). The symbol B indicates a relative barrier in the dissociation pathway. The symbol T indicates a two-electron transition in the dominant configuration is required to reach the adiabatic asymptote. Rydberg states are not included except for the d'Π, C'II, D'Σ⁺, and 1Π states and the multiplets lying above 10 eV. Otherwise the diagram is complete up to −12 eV (Hopper, 1984).
It has long been known that N$_2$O is a strong source of O($^1$S) following PID (photon impact dissociation). McEwan et al. (1974) demonstrated that the most prominent U.V. absorption band in N$_2$O (figure 6.2) which peaks at 129 nm (9.60 eV) is due to excitation from N$_2$O($X^1\Sigma^+$) to N$_2$O($D^1\Sigma^+$). The assignment D was made later by Hopper (1984) who calculated the X $\rightarrow$ D transition energy in the Frank–Condon region to be 9.9 ± 0.5 eV, in good agreement with experiment.

![U.V. absorption spectrum for N$_2$O from Zelikoff et al. (1953). It has also been confirmed by Rabalais et al. (1971).](image)

McEwan et al. (1974) and Black et al. (1975) have both measured the quantum yield of O($^1$S) from N$_2$O versus wavelength by observing the afterglow of the 557.7 nm line following photolysis of N$_2$O in a He buffer. Their results closely followed the absorption curve in figure 6.2, reaching a value very near unity at 129 nm. This was later confirmed by the calculations of Hopper (1984) which show that a relative potential barrier exists between the D state and adiabatic dissociation to N($^3$P) and NO($X^3\Pi$), thus the D state dissociates to N$_2$(X$^1\Sigma_g^+$) and O($^1$S) (see
Hopper (1984) reports that due to the diffuse nature of the D state and the required two electron transition during dissociation along the $N_2 - O$ asymptote, it is possible for the products to be in states other than $O(^1S)$ and $N_2(X^1Σ^+_g)$, but the fraction of these products must be small in light of the results of McEwan et al. (1974), and Black et al. (1975).

Regarding time-of-flight spectroscopy of dissociation products, $O(^1S)$ has been observed following PID of $N_2O$ at $λ < 135$ nm by Gilpin and Welge (1971) and at $λ = 130$ nm by Stone et al. (1976). The former group used a low work function surface to detect $O(^1S)$, while the second group used the chemi-ionization reaction

$$Sm + O → SmO^+ + e.$$  

Both groups obtained identical released kinetic energy (RKE) spectra. The latter results are shown in figure 6.3.

![Figure 6.3](image)

**Figure 6.3** RKE spectrum for $O(^1S)$ atoms following PID of $N_2O$ at 130 nm. Despite the low resolution, it is clear that the $N_2(X)$ fragments are vibrationally excited, as indicated by the arrows (Stone et al., 1976).
Regarding electron impact on \( \text{N}_2\text{O} \), \( \text{O}^1\text{S} \) has never been observed in a time-of-flight experiment. Other metastables have been reported. Two states of \( \text{N}_2 \) have been identified. Freund and Klemperer (1967) observed an \( \text{N}_2 \) state from electron impact on \( \text{N}_2\text{O} \) with a fragment kinetic energy distribution peaking at \(-0.3 \text{ eV}\), and an appearance potential of \( 8.7 \text{ eV} \). The process was probably

\[
e + \text{N}_2\text{O} \rightarrow e' + \text{N}_2\text{O}^* \rightarrow e' + \text{O}^3\text{P} + \text{N}_2(\text{A}^3\Sigma^*_u). \tag{6.2}
\]

This was confirmed later by Allcock and McConkey (1978), and more recently by Barnett et al. (1991). Gilpin and Welge (1971) also observed \( \text{N}_2(\text{A}^3\Sigma^*_u) \) with the same TOF structure in their photo-dissociation experiments. The parent state \( \text{N}_2\text{O}^* \) was not identified, but was possibly the linear \( \text{C}^1\Pi \) state since it is optically allowed and it is possible for a Rydberg state to dissociate via a non-adiabatic level crossing. There are nearby bent states of \( \text{N}_2\text{O}^* \) which can dissociate to the products in (6.2) as well (Hopper, 1984).

Clampitt and Newton (1969) reported an \( \text{N}_2^* \) fragment following EID (electron impact dissociation) of \( \text{N}_2\text{O} \) with a mean kinetic energy of \( 0.20 \text{ eV} \) and a threshold of \( 10.5 \text{ eV} \). They proposed they had observed either the process

\[
e + \text{N}_2\text{O} \rightarrow e' + \text{N}_2\text{O}^* \rightarrow e' + \text{O}^3\text{P} + \text{N}_2(\text{B}^3\Pi_g) \tag{6.3}
\]

followed by the cascade

\[
\text{N}_2(\text{B}^3\Pi_g) \rightarrow \text{N}_2(\text{A}^3\Sigma^*_u) + \text{hv}, \tag{6.4}
\]

or,
\[ e + \text{N}_2\text{O} \rightarrow e' + \text{N}_2\text{O}^* \rightarrow e' + \text{O}^{(3)P} + \text{N}_2(\text{a}^{1\Pi_g}). \] (6.5)

The former reaction (6.3) was later reported by Allcock and McConkey (1978) as a change in slope of the excitation function for \( \text{N}_2(\text{A}^{3\Sigma_u^+}) \), while the latter has been reported by Mason and Newell (1989). In that case, discrimination against \( \text{N}_2(\text{A}^{3\Sigma_u^+}) \) was made by using a high work function surface detector. No TOF observations of the metastable states \( \text{N}^{(2)D} \) or \( \text{N}^{(2)P} \) following EID or PID of \( \text{N}_2\text{O} \) have been published, though extensive data is available on the production of these species following photo-dissociation in buffer gas experiments (see e.g. Black et al. (1975) who reference earlier work).

Of all the metastable states of oxygen, only \( \text{O}^{(5)S} \) has been observed following EID of \( \text{N}_2\text{O} \) (Allcock and McConkey, 1978, Mason and Newell, 1989, Barnett et al. 1991). It is very energetic, appearing in TOF spectra with a broad FKE distribution reaching a maximum at 5 eV (figure 6.4).

![Figure 6.4](image)

**Figure 6.4** Fragment kinetic energy spectrum of \( \text{O}^{(5)S} \) fragments following electron impact dissociation of \( \text{N}_2\text{O} \) (Mason and Newell, 1989).
The process has been identified as

\[ e + N_2O \rightarrow 2e + N_2^-(B^2\Sigma_u^-) + O(5S) \]  \hspace{1cm} (6.6)

with an appearance potential of \(-29\) eV. \(+5S\) also arises from cascading from \(+5P\) since the \(\lambda = 777.4\) nm line is a prominent emission feature following electron impact on \(N_2O\) (van Sprang et al., 1978).

Allcock and McConkey (1978) have made the only study of the dissociation of \(N_2O\) using a rydberg detector. The lowest threshold for any rydberg production was \(15\) eV. The kinetic energy spectra for either \(N\) or \(O\) Rydbergs were very broad almost structureless distributions with energies ranging from 1 to 7 eV.

II. Time-of-flight and Released Kinetic Energy Spectra

On the following page (figure 6-5) are several time-of-flight spectra acquired at different electron impact energies. Their RKE transforms are displayed in figure 6.6. Each spectrum was acquired in one hour using a 1 \(\mu\)s pulsed electron beam at 2.5 KHz. The integrated current varied from 2 to 4 \(\mu\)A as the energy went from 30 to 300 eV. The reason for the variation is due to the high current used. The equivalent direct current would be 800 to 1600 \(\mu\)A, so space charge would begin to limit the flow at lower energies. The electron impact energies were measured directly from the filament bias supply (figure 4.3) and are expected to be accurate only to within a few volts because of the space charge in the interaction region. Calibration of the energy scale will be explained in the next section on excitation functions.
Figure 6.5 Time-of-flight spectra for $O^{(S)}$ fragments following electron impact dissociation of $N_2O$ at the incident electron impact energies indicated. In each case the line drawn below each spectrum represents the baseline from which the background can be determined. The intensities were current normalized and thus comparable to one another.
Figure 6.6  Released kinetic energy spectra obtained from the data of figure 6.5. The four curves have been normalized to unity at their maxima.
For the time-of-flight spectra of figure 6.5, the LG-595 red filter was used to observe the XeO\textsuperscript{+} fluorescence since the red emissions were the most intense (see chapter 5). Identical TOF spectra were obtained when the green and U.V. emissions were observed from the Xe layer, but with poorer statistical significance. These are shown in figure 6.7.

![TOF spectra](image)

**Figure 6.7** TOF spectra following EID of N\text sub{2}O by 100 eV electrons obtained by using a monochromator to select the XeO\textsuperscript{+} emission band of interest from the Xe layer. The vertical scales for each spectrum are not comparable.
From figure 6.7, it can be concluded that the same metastable fragment is responsible for all three emission features, provided that the same excitation function is obtained no matter which emission is observed. This is in fact the case, as demonstrated in the next section.

From the TOF spectra alone, it can be concluded that the fragment producing the three colour emission upon its arrival at the Xe layer 51 \( \mu \text{s} \) after electron impact is \( \text{O}^{(1S)} \) for the following reasons:

a) Comparison of the RKE spectra with the earlier work cited in the previous section rules out \( \text{O}^{(6S)} \), \( \text{O} \) Rydbergs, or any of the metastable or Rydberg \( \text{N}_2 \) states as the detected fragment.

b) The fragment cannot be a metastable or Rydberg \( \text{N} \) atom since no signal was observed when using pure \( \text{N}_2 \) as the target gas. \( \text{N}_2 \) does have many optically accessible states that dissociate to metastable or Rydberg \( \text{N} \) atoms (Black et al, 1975; Wells et al. 1976).

c) It cannot be metastable \( \text{N}_2\text{O} \) molecules because these would have a nearly Maxwell–Boltzmann TOF distribution reaching a maximum at 560 \( \mu \text{s} \).

d) \( \text{O}^{(1D)} \) or \( \text{O}^{(3P)} \) is not the fragment since it is energetically impossible for either to produce the green or U.V emission features. Neither can produce red emission when inserted in a Xe matrix. Only \( \text{O}^{(1S)} \) could produce all three emissions. See chapter 5.
e) High Rydbergs and ions were removed by the deflection plates. Low lying Rydbergs would have too short a lifetime to reach the detector in appreciable intensities.

g) The RKE spectra in figure 6.6 are all identical to the one obtained by Stone et al. (1976) for O(1S) produced by PID of N₂O (figure 6.3). The energy distribution is also in agreement with the PID experiment of Gilpin and Welge (1971).

h) The signal at 51 μs disappears when the plexiglass shutter (figure 4.1) covers the cold finger, but the prompt photons remain. Thus the signal must come from actual particles striking the Xe layer.

i) The fragment cannot be NO(a''II) because a combination of it and O(1S) would lead to a quartet state of N₂O. Excitation of such a state by electron impact would require a spin flip or electron exchange resulting in a E⁻³ O(1S) intensity dependence past threshold, which is clearly not the case.

The TOF structure of O(1S) has the same shape regardless of the electron impact energy. This is quite different from what is normally observed (e.g. see the O(1S) TOF spectra from CO₂ in chapter 8) as increasing the electron energy usually opens up new production channels for the metastable species under investigation by exciting higher lying molecular states, each having a separate excitation curve. Thus there is almost certainly one production channel which leads to the O(1S) distribution seen in figure 6.5, and that is via excitation of the N₂O D state. This conclusion is supported by the very smooth shape of the excitation function (figure 6.12) in the
near threshold region. No evidence of additional channels for O(1S) production were observed.

The smaller structure that can be seen at 30 μs in the 100 eV TOF spectrum is shown below in figure 6.8 on a magnified scale. An investigation revealed that it was most intense in the 70-80 eV range of electron impact energy. This may be interpreted as O(1S) production via some higher lying parent state of N₂O. It is possible that these O(1S) atoms arise via cascade from the O(3s⁺ 1P^0) state. The O(3s⁺ 1P^0) → O(1S) transition (121.8 nm) has not been reported following EID of N₂O, but has been observed following EID of O₂ (James et al. 1988).

![TOF spectrum](image)

**Figure 6.8** TOF spectrum at 100 eV from figure 6.5 with magnified vertical scale. A solid line has been drawn to guide the eye.

The good agreement of the RKE spectra of figure 6.6 with that of Stone et al. (1976) indicates that the time between the arrival of the O(1S) at the Xe surface
and photon emission is of the order of 1 μs. Like the data of Stone et al. (1976), the
dissociation takes place from a state that is repulsive in the Franck-Condon region,
and there is clearly some degree of vibrational excitation in the undetected N₂
fragments.

Some idea of the relative vibrational population of the undetected N₂
fragments was obtained from a long scale TOF spectrum (figure 6.9 (a)). Once the
sloping background due to the TAC deadtime was subtracted (see chapter 4, section
IV, part b), the RKE spectrum was calculated (figure 6.9 (b)). The shape of the
potential surface of the N₂O D state in the Franck–Condon region can be deduced
from the absorption spectrum in figure 6.2. From this one can calculate, to a good
approximation, the RKE distribution if the N₂ molecule remains in its ground state.
This distribution can be qualitatively represented by a gaussian function and is shown
in figure 6.9(b) as the dashed line.

Using many of these gaussian functions shifted towards lower energies by
increments equal to the vibrational energy levels of N₂, and applying a weighting
factor to each one, a qualitative fit to the RKE data of figure 6.9 (b) can be
obtained. It is shown as a solid line. The weighting factors are shown in the inset to
figure 6.9 (b) and represent the distribution of vibrational states of the undetected
N₂ fragment. The results are similar to that of Stone et al. (1976), in figure 6.3. They
were unable to observe the higher vibrational states because of their low signal to
noise ratio.
Figure 6.9

(a) A long scale TOF spectrum from N₂O at 100 eV electron impact energy. The vertical scale is magnified in order to show the signal at longer flight times. (b) The RKE distribution. The dashed curve represents the theoretical RKE distribution if there were no vibrational excitation of the N₂ fragment. The solid curve represents the fit to the data using the N₂ vibrational population shown in the inset.
The distribution resembles a Poisson distribution, which is predicted by a semi-classical theory of dissociation (Holdy et al., 1970). A full quantum mechanical treatment is available (Band and Freed, 1975) but it has not been applied. It is likely that there is distortion on the very low energy side of the RKE spectrum because of the effect of the parent molecule thermal velocity on the O atom fragments.

No attempt was made to ascertain the rotational excitation of the undetected N₂ fragments. Holdy et al. (1970) have reported that following photolysis of ICN, which remains linear in the excited parent dissociating state, the energy released was partitioned in the following manner; translational \( \rightarrow \) vibrational \( \rightarrow \) rotational.

As a check to ensure that the O\(^1\)S observed was the result of single collisional excitation of N₂O to the D state, and that no secondary processes were involved (such as multiple collisions), metastable signal versus electron beam current \( I \), and source pressure \( P \), were plotted and are shown in figure 6.10 (a) and (b) respectively. The curvature in the O\(^1\)S versus pressure plot arises from a non-linear N₂O flow increase in the capillary tube.

At beam currents approaching 2 mA there was a marked departure from linearity for the O\(^1\)S intensity (not shown). All crucial measurements, such as excitation curves, relative flow comparisons, etc., were done in the linear region. The slight dependence of the background on both current and pressure was probably due to the arrival of relatively small amounts of very slow O\(^1\)S at the Xe surface.
III. Appearance Potential and Calibrated Excitation Function

Excitation functions for O(1S) production following EID of N₂O were obtained at low electron beam currents which remained nearly constant from 8 eV up to 1000 eV (e.g. see figure 4.4). At low current, the electron impact energy is well defined, unlike the energies at the high currents used to acquire TOF spectra.
The biggest problem with excitation functions, particularly for obtaining thresholds, is to calibrate the energy scale. As discussed in chapter 4, the energy of the electrons in the collision volume defined by the intersection of the electron beam, gas jet, and field of view of the detector is not simply the voltage bias of the filament. A means to calibrate the energy scale under the conditions present during the acquisition of excitation functions was devised by using the prompt photons. Figure 6.11 shows the optical spectrum for the prompt photons produced following electron impact excitation of \( \text{N}_2\text{O} \).

![Optical spectrum of prompt photons from \( \text{N}_2\text{O} \). This was taken at 100 eV electron impact energy, using the monochromator with 1 nm resolution. The spectrum has not been corrected for variations in sensitivity of the monochromator–photomultiplier combination. Note the magnification factor of 10 applied above 500 nm.](image)

The intense U.V. bands between 330 and 400 nm arise from transitions between different vibrational levels of the excited ion state \( \text{N}_2\text{O}^+(A^2\Sigma^+) \) to the different vibrational levels of ground state ion state \( \text{N}_2\text{O}^+(X^2\Pi_i) \). These will be referred to as the A–X bands hereafter. Several other features in the spectrum are
notable, namely the lines at 777 and 845 nm which are from the atomic oxygen transitions $^5P - ^5S$ and $^3P - ^3S$ respectively, and the line at 822 nm from the atomic nitrogen transition $^4P_0 - ^4P$. The atomic fragments arise from dissociation of N$_2$O. Absolute cross sections for the atomic lines and the A−X bands have been measured by van Sprang et al. (1978).

The line at 355.8 nm is a transition from the A (000) to the X (000) vibrational level, and thus has the lowest threshold of the U.V. bands at 16.38 eV (sum of the ionization potential plus transition energy). Thus, calibration of the energy scale is made by placing a U.V. filter (UG-11, transmission curve in figure 4.7) in front of the photomultiplier and observing the threshold for the prompt photons. Van Sprang et al. (1978) report a weak broad band emission from electron impact on N$_2$O in the 220−330 nm range which is due to the NO($B^2Π - X^2Π$) transition. It has a lower threshold (15 eV) than the A−X bands, but its intensity is about factor of 10 less, so it has a negligible contribution to the prompt photon threshold observed with the U.V. filter.

The method to obtain appearance potentials and excitation functions with calibrated energy scales goes as follows. Once the experiment is set up and stable, an excitation function of the metastable signal is obtained, usually using the red emissions. This requires about 10 to 20 hours in order to get good statistics. The TAC is gated according to the method described in chapter 4 to cover the 50−150 μs range. Then, without changing any conditions, the red filter (LG-595) is replaced by the U.V. filter (UG-11), and the TAC gate is switched to cover the range from 0
to 20 \, \mu s to include all of the prompt photon signal, and its excitation function is acquired. This usually requires about 10–30 minutes because of the intensity. Checking the prompt photon excitation function before the metastable threshold indicated that very little drift took place over to 10 to 20 hour time span.

In order to increase the signal to background ratio, 20 \, \mu s long electron pulses were used in all of the O(^1S) excitation functions from N\textsubscript{2}O, at a repetition rate of 2.5 \, KHz. The filament operating current was typically 5.5 A yielding a collected current of about 5 \, \mu A on the faraday cup (biased at +50 V) for an input pressure of 10 torr. The outer cup was biased at +10 V.

Even though it was not possible to regulate the cold finger temperature over long periods of time, the excitation functions are immune to the effects of changing detection efficiency and other long time scale drifts because each sweep of the multi–channel scaler took only 5 minutes. Drifts in the voltages applied to the electron gun would smear the threshold, but as mentioned already, this effect was negligible over a 24 hour time span.

Threshold excitation functions of the metastable signal were obtained with either the red or U.V. filter in place and are shown in figure 6.12. Also shown is the prompt photon excitation curve. It was not possible to determine the threshold of the metastable signal using the green emission due to its low intensity.
Figure 6.12  Threshold excitation functions for O(^1S) from EID of N₂O using either the red or U.V emission from the Xe layer. The prompt photon is threshold is also shown. In each case, the ramping voltage went from 0.2 to 51.2 V in steps of 0.2 V. The curves are not current-normalized.

It is evident from figure 6.12 that a gradual onset for O(^1S) production occurs with a threshold near 10 eV when either the U.V. or red emissions are observed. This is further evidence that both emissions are produced by the same metastable state impacting on the Xe layer. Both curves are identical in shape as well. The gradual onset is the result of the convolution between the spread in energy of the electron beam (which is about 1 eV) and the actual threshold curve.
The lack of any sudden change in the slope of the metastable excitation curve after the threshold concurs with what was observed in the TOF spectra; there is one dominant channel for production of O(1S) following EID of N₂O. The threshold of 10 eV indicates that dissociation is taking place from the D state of N₂O (figure 6.1).

A current-normalized excitation function for the production of O(1S) following EID of N₂O for energies up to 1000 eV is shown in figure 6.13 (a). Also shown in 6.13 (b) is the prompt photon excitation curve which has been normalized to unity at its maximum, along with the normalized cross section data from van Sprang et al. (1978) for excitation of the complete A–X system. The good agreement between the two data sets indicates the quality of the electron beam characteristics.

From a current-normalized curve for O(1S) production in the 0-100 eV range, the maximum was determined to be at about 45 eV, but the maximum is fairly flat. The shape of the curve after the maximum, figure 6.13 (a), is typical of an optically allowed transition, indicating again that the D state of N₂O is largely responsible for the production of O(1S). The calibration of the vertical scale in units of the total cross section was obtained by using the Bethe-Borne approximation as described in chapter 3 (equation 3.15).

The Fano plot used to determine the constant \( Cn \) in equation 3.15 is shown in figure 6.14. The straight line was a fit to the data above 500 eV after a 5 point smoothing procedure had been applied. A linear regression procedure found in commercially available software calculated an X intercept of 71.2 ± 11.9 eV. Several other excitation curves fell within the same range and the value 71.2 eV was adopted
Figure 6.13  (a) Calibrated excitation curve for O(^1S) production from N_2O for electron energies up to 1000 eV. (b) Excitation function of N_2O A-X bands. The squares are from the data of van Sprang et al. (1978). Both data sets were normalized to unity at their maxima.
as the average. The result is a value for $Cn$ of $0.0478 \pm 0.0079$. Using a value for the oscillator strength $f_n = 0.360 \pm 0.007$ for the D state which is the average of several different measurements (Zelikoff et al., 1953, Rabalais et al., 1971, and Heubner et al., 1975), the total cross section for production of the $O(^1S)$ state from $\text{N}_2\text{O}$ was calculated at 1000 eV to be $\sigma = 6.49 \pm 0.43 \times 10^{-18}$ cm$^2$.

Figure 6.14  Fano plot of excitation curve data from figure 6.13(a). The data has had a five point smooth applied to it. The straight line was obtained from a linear regression analysis of the data above 500 eV. Its X intercept is $71.2 \pm 11.9$ eV.
Despite the large error in the X intercept, it has a relatively small effect on the calculated cross section as the factor \( C \) appears inside the logarithm term for the total cross section in equation (3.15). The total cross section from threshold to 1000 eV for \( O(^1S) \) production from EID of \( N_2O \) has been tabulated in table 6.1. This was done by drawing a smooth curve fit by eye through the data of figure 6.13 (a), and a current normalized 0-100 eV excitation curve, normalizing both to the calculated cross section at 1000 eV. The relative error in the cross sections was better than 10%. It was estimated that the contribution of the fast fragment at 30 \( \mu s \) (in figure 6.8) and the slower \( O(^1S) \) fragments that were not included in the gated window during data acquisition was less than 0.5 %.
Table 6.1  Integral cross section for production of O($^1$S) following electron impact dissociation of N$_2$O.

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Chapter 7

The Results Obtained from Oxygen

I. Review of Earlier Work

A review of photon or electron impact excitation studies on \( \text{O}_2 \) has been presented by Itikawa et al. (1989). Complete TOF studies of metastable production following EID of \( \text{O}_2 \) have been performed by Freund (1971), Borst and Zipf (1971), and recently by Mason and Newell (1990). All three experiments detected only \( \text{O}(^5\text{S}) \) atoms or \( \text{O} - \text{Rydbergs} \). The results (figure 7.1 a) reveal two ranges of arrival times for \( \text{O}(^5\text{S}) \) in TOF spectra. There is a slow group with a released kinetic energy distribution peaking at \(-1\) eV that clearly shows dissociation taking place from the repulsive wall of a bound state. That process has an onset at \(14.5\) eV and is attributed to
\[ e + O_2 \rightarrow e^* + O_2^* \rightarrow e^* + O(^3P) + O(^5S) \quad (7.1) \]

The dissociative \( O_2^* \) state has been identified as \( ^3\Pi_u \). At impact energies greater than 15.9 eV, \( O(^5P) \) is produced creating a second contribution to the slow \( O(^5S) \) arrival times via the cascade

\[ O(^5P) \rightarrow O(^5S) + \lambda(777\text{nm}) \quad (7.2) \]

A fast group of fragments appears at electron impact energies greater than 20.5 eV and dominates the slower group at higher impact energies. Its released kinetic energy distribution changes significantly with increasing electron impact energy, spanning the range 2-15 eV at 60 eV electron impact energy. Its shape suggests that this group arises from purely repulsive states. The identity of these parent dissociative states of \( O_2 \) is still unclear (Mason and Newell, 1990).

Recent measurements by Erdman and Zipf (1987) on the doppler broadening of the \( ^5P \rightarrow ^5S \) (777 nm) multiplet following EID of \( O_2 \) indicate \( O(^5P) \) kinetic energies in agreement with the slow and fast range of kinetic energies from the TOF data of \( O(^5S) \). Thus cascading contributes to the faster \( O(^5S) \) fragments as well.

Freund (1971) has made the only report of \( O \rightarrow \) Rydberg production following EID of \( O_2 \). In that work, high Rydberg states of \( O \) were detected by collisions with \( SF_6 \). The high electron affinity of \( SF_6 \) would ionize the Rydberg atom, which could subsequently be detected by an electron multiplier. The detector was placed close to (17 cm) the interaction region in order to detect Rydbergs of the lowest possible
since the lifetime of a Rydberg atom with fixed orbital angular momentum is proportional to $n^3$.

**Figure 7.1** Released kinetic energy distributions for (a) slow and fast O(\(^3\)S) atoms, and (b) O–Rydbergs following EID of O\(_2\) (Freund 1971). The arrows refer to dissociation channels.

Figure 7.1 (b) shows the RKE distributions obtained by Freund for the slow and fast O–Rydbergs at different electron impact energies. The O-Rydberg RKE spectrum is more complicated because of the lack of selectivity in the detector, and the many production channels possible. The excitation curve for Rydberg production
from EID of $O_2$ has a threshold at 21 eV, with distinct breaks in the slope at 24, 26, 31, 38 and 44 eV.

Stone et al. (1975) reported a TOF spectrum for oxygen atoms produced by electron impact on $O_2$ (figure 7.2). Their method of detection has already been described in the previous chapter. The TOF data indicates an FKE distribution between 0.2 and 1.0 eV with a maximum at 0.7 eV that can be attributed to the process

$$e + O_2 \rightarrow e' + O_2(B^3\Sigma_g) \rightarrow e' + O(^3P) + O(^1D).$$  \hspace{1cm} (7.3)

They also observed some structure on the TOF spectra at shorter flight times which

![TOF spectrum of atoms following EID of $O_2$. The solid lines are predicted TOF spectra for the Schumann–Runge dissociation processes (Stone et al., 1975).](image)

Figure 7.2
could not be resolved. They have attributed it partly to a parent state which
dissociates to two ground state \( \text{O}(^3\text{P}) \) atoms. Both processes come from the same
parent states of \( \text{O}_2 \) that are responsible for the Schumann–Runge absorption
continuum in the U.V. Since the potential curves are well known (Gilmore, 1965)
they were able to calculate the TOF distributions for \( \text{O}(^1\text{D}) \) and \( \text{O}(^3\text{P}) \). These are
shown as the solid lines in figure 7.2, indicating an excellent fit to the data. At
shorter flight times, other detected fragments may have been \( \text{O}(^1\text{S}) \) and \( \text{O}(^5\text{S}) \). One
disadvantage of the detection system used by Stone et al. was that it was sensitive to
\( \text{O} \)-atoms in a variety of states, both ground and excited. Stone et al. (1976) also
carried out photo-dissociation experiments using a pulsed photon source. They
demonstrated that for wavelengths in the Schumann–Runge continuum the TOF
spectra were identical to figure 7.2, except the signal at shorter flight times was not
observed. Shafer et al. (1991) have duplicated the \( \text{O}(^1\text{D}) \) kinetic energy distribution
of Stone et al. (1976) following PID of \( \text{O}_2 \). They, however, used resonance enhanced
multi-photon ionization by intense laser light to detect \( \text{O}(^1\text{D}) \) atoms.

Lawrence and McEwan (1973) detected weak \( \text{O}(^1\text{S}-^1\text{D}) \) emissions from PID
of \( \text{O}_2 \) in a buffer gas. They reported a quantum efficiency of 0.1 at 105 nm (11.8 eV).
The most up to date potential curve calculations indicate they must have been
exciting the \( ^1\Sigma_u^+ \) state of \( \text{O}_2 \) which dissociates to \( \text{O}(^1\text{S}) \) and \( \text{O}(^1\text{D}) \) (see figure 7.12).
The fact that the transition is spin forbidden explains the small \( \text{O}(^1\text{S}) \) intensity.

The only other study of metastable production following EID of \( \text{O}_2 \) was that
of Kiefl et al. (1983). They employed a solid Xe layer detector (as mentioned earlier
in chapter 5) to selectively detect O(^1S) atoms following EID of O_2. Their TOF spectra (figure 7.3) revealed the presence of two processes in which slower fragments were the dominant. They did not produce any kinetic energy spectra but it was possible to deduce from their data that the majority of the fragments had kinetic energies around 3 eV. They measured extinction cross sections for O(^1S) collisions with a variety of target gases, and subsequently discontinued their work. As mentioned in chapters 1 and 5, it was their work which instigated further development of the Xe layer detector which is the subject of this dissertation.

![TOF spectrum of O(^1S) atoms following EID of O_2 at 130 eV (Kiefl et al. 1983).](image)

**Figure 7.3** TOF spectrum of O(^1S) atoms following EID of O_2 at 130 eV (Kiefl et al. 1983).
II. Time-of-Flight and Released Kinetic Energy Spectra

TOF spectra obtained using oxygen as the target gas are shown in figure 7.4 for various electron impact energies. In each case, the red filter was placed in front of the photomultiplier. The corresponding released kinetic energy transforms are shown in figure 7.5. Below 4 eV the $t^3$ factor in the transform exaggerates the noise in the background of the TOF spectra.

In contrast to the O(1S) TOF distributions from N$_2$O presented in the previous chapter, the intensity of the metastable signal for comparable source conditions (10 torr pressure, 1 µs electron pulses at 5.0 KHz, 1–3 µA of current) was about an order of magnitude less. Consequently, each TOF spectrum in figure 7.4 required 16 hours of data acquisition. Like the data from N$_2$O, the emissions produced following the impact of the O–metastable on the Xe layer in the 20-55 µs range of figure 7.4 are predominantly red with a weaker U.V. component, see figure 7.6. The green component is extremely weak. It can be seen, but is very noisy.

The primary feature of the TOF spectra is the sharp peak at 41 µs. A second less intense feature is observed as a shoulder on the short TOF side of the main peak. It appears at energies greater than 30 eV, but never rises to more than a quarter of the intensity of the first. A possible third feature is a slight shoulder on the long TOF side of the primary peak which manifests itself more clearly in the RKE spectra at around 5 eV.
Figure 7.4 Time-of-flight spectra for O(1S) fragments following electron impact dissociation of O$_2$ at the incident electron impact energies indicated. The baselines have been drawn for in each spectrum in order to determine the background. The vertical scales are not comparable for each spectrum.
Figure 7.5  Released kinetic energy spectra obtained from the data of figure 7.4. The four curves have been normalized to unity at their maxima.
Figure 7.6  TOF spectra obtained from EID of $O_2$ using the red or u.v. emissions from the Xe layer. The vertical scales are not comparable. In both cases, 5 $\mu$s electron pulses were used.

The RKE spectra illustrate that dissociation must be taking place from purely repulsive states in $O_2$. There is a minimum of approximately 4.0 eV of energy released in the dissociation, which would put the threshold for the process
The fast fragment appears as a high energy tail in the kinetic energy spectra extending up to 15 eV at the higher incident energies. This indicates that contributions are occurring from high-lying parent O\textsubscript{2} curves which are steeply repulsive in the Franck-Condon region. Identification of the parent O\textsubscript{2} states will be made following examination of the excitation function data in the next section.

On the basis of the foregoing observations, it can be concluded that the metastable fragment responsible for the structure between 20 and 55 \(\mu\)s is O\(^{(1)S}\) produced by EID of O\textsubscript{2} for the following reasons:

(a) The TOF spectra and their RKE transforms just shown are unlike those obtained using other detection methods, and so O\(^{(2)S}\), O\(^{(1)D}\) and O–Rydbergs can be ruled out by comparison.

(b) The deflection plates remove unwanted ions. In fact there was no difference in the metastable count rate when one plate was toggled between ground and 5000 V. The magnetic field alone was sufficient to prevent ions from reaching the Xe layer.

(c) Closing the plexiglass shutter (figure 4.1) eliminates the metastable signal, but the prompt photons remain.

(d) Metastable O\textsubscript{2} molecules cannot be responsible since they would appear around 475 \(\mu\)s in the TOF spectra.
The emission spectrum from the Xe layer is essentially identical to that obtained using N₂O targets where O(^1S) was responsible.

The prompt photon signal in each TOF spectra arises from numerous sources of excitation, but is predominantly radiation from the 1st negative bands of O₂⁺ (b^1Σ⁺ \rightarrow a^3Π_u, (490 nm < \lambda < 750 nm), and the 5P \rightarrow 5S (\lambda = 777.4 nm) and 3P \rightarrow 3S (\lambda = 844.7 nm) transitions of atomic oxygen arising from dissociative excitation. An optical emission spectrum of the prompt photons is shown in figure 7.7.

![Optical spectrum of the prompt photons produced by 100 eV electron impact on O₂. The resolution is 1 nm. The spectrum has not been corrected for variations in sensitivity with wavelength of the photomultiplier–monochromator combination.](image)

The background in the TOF spectra is mostly due to scattered light from the hot filament, with a small contribution from the photomultiplier dark count. However, there was also a component to the background which appeared to be due to some U.V. photon or metastable since closing the plexiglass shutter (400 nm cut
off) eliminated it, but left the filament background. By using various filters and toggling the shutter, it was determined that the background emissions were strongest in the violet region of the spectrum, and very weak in the red.

This was different from the background observed in the TOF spectra from N₂O. In that case, the background was strongest in the red, and weaker in the U.V. Thus, it was likely caused by very slow O(^1S) atoms reaching the detector. Long scale TOF spectra using 20 μs electron pulses revealed no structure beyond 55 μs. The background was slightly sloped possibly due to a TAC dead time effect. This background component from O₂ displayed an excitation function peaked at a somewhat higher energy than for the O(^1S) atoms responsible for the TOF structure between 20 and 55 μs (see the next section).

It is clear that the TOF spectra demonstrate the complete insensitivity of the Xe layer to O(^1D). O₂ produces copious O(^1D) following electron impact (figure 7.2). O(^1D) atoms would appear beyond 55 μs in our apparatus, but as already mentioned, no structures exists after that point. This verifies the theoretical prediction of Maillard et al. (1983) that O(^1D) in a Xe matrix undergoes a radiationless transition to the ground state. The fate of O(^5S) atoms reaching the Xe layer is a matter of speculation. It is not known whether they form some high lying excimer state with Xe. If the O(^5S) atoms de-excite during thermalization, the resulting V.U.V. radiation would not be transmitted by the quartz windows. The energy dumped into the Xe layer by the O(^5S) atoms, and by V.U.V. photons following electron impact
might be responsible for the background emissions, but this seems unlikely since the
effect was not observed with N₂O.

Measurements of $O(^1S)$ intensity versus electron beam current and source
pressure were made and are shown in figure 7.8. In the case of intensity versus
current, taken at 10 torr source pressure, the $O(^1S)$ intensity is clearly linear. Higher
currents were not possible when operating the electron gun in the $O_2$ atmosphere.
All critical measurements were done in this linear region. The signal versus pressure
curve was taken at an equivalent direct current of 720 $\mu$A. Note that in the signal
versus current curve the red filter (LG–595) was used and the background is
practically flat. This was not the case in the violet region of the spectrum. The
background was also dependent on pressure as well, shown in figure 7.8(b) where no
filter was in place.
Figure 7.8  
O(^1S) intensity (circles) versus electron beam current (a), and source pressure (b). Also shown is the background (triangles) and the prompt photon intensity (squares). For (a), the red filter (LG-595) was in place; while for (b), no filter was used.

III. Appearance potentials and Excitation Functions

A threshold excitation function for the production of all metastable fragments is shown in figure 7.9 using the red XeO* emission. As in the work with N₂O, 20 μs electron pulses were used in order to achieve an adequate signal to noise ratio. The TAC was gated to span a 30 to 75 μs range following the electron pulse to include the entire range of O(^1S) arrival times. Electron beam currents were kept in the low
linear operating region. Acquisition times were about 24 hours long in order to get good statistics.

Calibration of the energy scale was obtained by observing the threshold for the prompt photons of the first negative bands (also shown in figure 7.9) through the P70–550 green filter. The method has already been described in chapter 6. Because the transmission of the filter (figure 4.7) strongly attenuates the signal from the (0,0) vibrational band of the $O_2^+(b^4\Sigma_g^+ \rightarrow a^4\Pi_u)$ at 603 nm, the threshold is due to the very strong (1,0) transition at 563 nm. This band has an appearance potential of 18.32 eV. For the (0,0) transition it is 18.21 eV (Huber and Herzberg, 1979). This puts the onset for the metastable signal at 14.0 ± 0.5 eV, which is in good agreement with the threshold calculated from the RKE spectra of Figure 7.5 assuming that the two fragments produced are $O(3P)$ and $O(1S)$. It was not possible to measure thresholds for fragments of different kinetic energies to an adequate precision because of the low intensity of the $O(1S)$ signal near threshold.

Unlike the results for $N_2O$, obtaining a threshold curve from the U.V. emissions released following $O(1S)$ impact on the Xe layer was not possible. This was partly because of its weak intensity, but mostly because the background emissions dominated the signal. Thus, the excitation curve near threshold taken with the U.V. filter in place (also shown in figure 7.9) has a different shape than the one taken with the red filter. The excitation curve for the background emission appears to have the same threshold as the one for $O(1S)$, but it reaches a maximum at about 130 eV (not shown), whereas the $O(1S)$ excitation curve reaches a maximum at 80 eV (figure 7.10).
Figure 7.9 Excitation functions taken near threshold for the O(1S) atoms arriving in the 20–55 μs range using the red or U.V. emissions. Also shown is the excitation curve for the emission of prompt photons from the O₂ 1st negative bands. The vertical scales are not comparable.

This is clearly different from the case with N₂O (previous chapter) where excitation functions using the red or U.V. emissions had identical thresholds and shapes.

An excitation function from threshold to 1000 eV for O(1S) using the red filter is shown in figure 7.10 (a). Figure 7.10 (b) is the excitation function for the 1st negative bands viewed through the green filter. It has been normalized to unity and plotted against the normalized cross section data for the (1,0) transition as measured by Borst and Zipf (1970). There is excellent agreement between the two data sets again demonstrating the excellent uniformity of the electron beam over the large energy range.
Figure 7.10  (a) Calibrated excitation curve for O(^1S) production O₂ for electron impact energies up to 1000 eV. (b) Relative cross section for 1st negative bands of O₂ up to 1000 eV. The squares are from the data of Borst and Zipf (1970).
The vertical scale of figure 7.10 (a) was calibrated in units of the absolute integral cross-section using the relative flow technique. Basically, the O(1S) signal from N₂O was used as a standard, and comparisons were made between the two gases after signals had been normalized to unit target density and unit beam current. This technique was described in chapter 3. There it was shown that the total cross section for O(1S) production from O₂, $\sigma_{O₂}$ is given by the relation

$$\sigma_{O₂} = \sigma_{N₂O} \frac{I_{N₂O}}{I_{O₂}} \frac{N_{N₂O}}{N_{O₂}} \frac{R_{M(O₂)}}{R_{M(N₂O)}} ,$$

(7.5)

where $I$, $N$, and $R_M$ are the appropriate electron beam current, target gas density and recorded metastable count rate respectively. The procedure for evaluating the target gas density ratio has been discussed in detail in chapter 3. Prompt photons for either the N₂O⁺ A-X bands or the O₂⁺ first negative bands were used to provide a monitor of the relative gas densities. These emissions met the qualifications discussed in chapter 3. It was assumed that the photon count rate was directly proportional to the source density. The data for the two gases is shown in figure 7.11. Molecular flow occurred for both gases at source pressures less than 0.1 torr. The absolute pressure measurements required the use of two Baratron Gauges (0.5% accuracy) connected simultaneously in order to span the wide pressure range with significant precision.

A measurement of the O(1S) count rate $R_M$ had to be made for both N₂O and O₂ targets under identical Xe layer conditions. This was done by using a counter gated over the time interval 20 to 80 µs to include all of the metastable signal. The red filter (LG-595) was in place during this procedure. A second counter was gated
Figure 7.11  Photon count versus source pressure for (a) N₂O, and (b) O₂. See text for more details.
from 850 to 910 \( \mu s \) to count the background. A third counter was gated to record only the prompt photons. Electron pulses were 5 \( \mu s \) long at 1.0 KHz at an impact energy of 100 eV.

First \( \text{N}_2\text{O} \) was used as the target with a certain source pressure (\( \sim 10 \) torr) and electron beam current (\( \sim 5 \mu \text{A} \)). Several metastable counts were made. Then the \( \text{N}_2\text{O} \) was replaced by \( \text{O}_2 \) as the target gas at similar source pressure. The beam current was monitored and several metastable counts were obtained. The \( \text{O}_2 \) was shut off and the procedure repeated using \( \text{N}_2\text{O} \), then \( \text{O}_2 \) and so on, being sure to return to the same source pressure for that particular gas each time. When this was done, the current and prompt photon count rate were repeatable each time. The cold finger temperature and Xe flow was monitored closely to ensure their stability during data acquisition.

After the first cycle of gases, the metastable count (less the background) had increased 20\% from the first \( \text{N}_2\text{O} \) run. This was probably due to some surface effect due to exposure of the Xe surface to \( \text{O}_2 \). Afterwards the \( \text{O}(1\text{S}) \) counts were repeatable after each cycle, which indicates that the Xe surface had stabilized and thus it can be assumed that it had the same conversion efficiency for \( \text{O}(1\text{S}) \) from either the \( \text{O}_2 \) or \( \text{N}_2\text{O} \) target gases.

Using the average \( \text{O}(1\text{S}) \) count rates \( R_M \) (counts per second), and currents \( I \) for the target gases from these alternating source gas measurements, and calculating the target gas density ratio by linear interpolation of the data from figure 7.11 together with equation (3.22), the value for the cross section for \( \text{O}(1\text{S}) \) production
from EID of $O_2$ was calculated to be $2.04 \pm 0.36 \times 10^{-18} \text{ cm}^2$ at 100 eV using the value for the cross section from $N_2O$ at the same energy (from Table 6.1).

The uncertainties in the count rates were kept to less than 2% by using adequately long counting times. Other uncertainties in measured quantities were smaller due to the accuracy of the instruments used. The largest uncertainty came from the calculation of the relative number densities in the interaction volume (e.g. see Lucas, 1973), which was estimated at approximately 11%. At the moderately high currents used, the beam energy in the interaction region is probably not exactly 100 eV due to space charge depression. The error introduced by this, however, is small because both excitation curves are fairly flat around 100 eV. The uncertainty of the cross section from $N_2O$ itself is 10% (see chapter 6). The result of all these factors, some estimated and some measured, results in an overall uncertainty in the cross section for $O(^1\text{S})$ production from $O_2$ at 100 eV of $\pm 18\%$. The total cross section from threshold to 1000 eV has been tabulated in Table 7.1 by drawing a smooth curve fitted by eye through the raw data, figures 7.9 and 7.10 (a), and normalizing it to the cross section at 100 eV.

Note that in using this relative flow method it has been assumed that the ratio of the attenuation coefficients (see equation 3.16) for both $N_2O$ and $O_2$ target gases and $O(^1\text{S})$ is nearly unity.
Table 7.1  Integral cross section for production of O(1S) following electron impact dissociation of O\textsubscript{2}.

<table>
<thead>
<tr>
<th>E (eV)</th>
<th>(\sigma) (10(^{-18}) cm(^2))</th>
</tr>
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<tbody>
<tr>
<td>14</td>
<td>threshold</td>
</tr>
<tr>
<td>16</td>
<td>0.35</td>
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<tr>
<td>20</td>
<td>0.92</td>
</tr>
<tr>
<td>24</td>
<td>1.26</td>
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<tr>
<td>28</td>
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<td>32</td>
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<tr>
<td>36</td>
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<td>40</td>
<td>1.82</td>
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<tr>
<td>45</td>
<td>1.92</td>
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<tr>
<td>50</td>
<td>2.00</td>
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<td>60</td>
<td>2.02</td>
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<td>70</td>
<td>2.06</td>
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<td>120</td>
<td>1.98</td>
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<tr>
<td>140</td>
<td>1.90</td>
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<td>160</td>
<td>1.82</td>
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<tr>
<td>180</td>
<td>1.75</td>
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<tr>
<td>200</td>
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<td>600</td>
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<td>700</td>
<td>0.82</td>
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<tr>
<td>800</td>
<td>0.75</td>
</tr>
<tr>
<td>900</td>
<td>0.69</td>
</tr>
<tr>
<td>1000</td>
<td>0.65</td>
</tr>
</tbody>
</table>
Note that it was also assumed that the detection efficiency of the Xe layer was independent of \( \text{O}^1\text{S} \) velocity. An attempt to check this by comparing the measured \( \text{O}^1\text{S} \) signals with the prompt photon signals, for which some of the excitation cross sections are known resulted in inconclusive results due to the large errors involved in extracting the total cross sections for all prompt photon production in the spectral range covered by the red filter. In principle this should give an internal reference for each target gas.

It is expected that there will be very little velocity dependence, since all \( \text{O}^1\text{S} \) atoms impacting the layer will eventually be thermalized inside the matrix and form the radiating \( \text{XeO}^+ \) excimer. However, the time taken to thermalize may be velocity dependent, and some evidence for this was found when constructing the repulsive curve in the Franck–Condon region for the parent dissociating state, see the next section.

In addition to the last point, an isotropic distribution of the \( \text{O}^1\text{S} \) fragments was also assumed. As discussed earlier (Section 2.V), this assumption will be valid at higher electron impact energies. Near threshold, it may not hold strictly depending on the number and symmetries of the contributing repulsive bound states.
IV. Identification of the Parent O₂ States Responsible for the TOF Spectra

The ground state of O₂ is $^3\Sigma_g^\text{−}$. There are 11 states of O₂ that are possible when combining O($^1\text{S}$) with O($^3\text{P}$), O($^1\text{D}$), or O($^1\text{S}$). The excitation curve in figure 7.10 (a) has a shape which is typical of an optically allowed transition. Thus, the states arising from O($^1\text{S}$) + O($^1\text{S}$), and O($^1\text{S}$) + O($^1\text{D}$) can be excluded since these form singlet O₂ states (Herzberg, 1950) and triplet to singlet excitation would require a spin flip or electron exchange. These type of cross sections have a sharply peaked maximum within a few eV of threshold, with a rapid fall off at higher energies. This is clearly not the case (figure 7.9) so the dominant states must be triplet. This leaves O($^1\text{S}$) + O($^3\text{P}$), which can form four possible states; $^3\Sigma_u^\text{−}$, $^5\Pi_u$, $^4\Sigma_g^\text{−}$, and $^5\Pi_g$ (Saxon and Liu, 1977). Since optically allowed transitions are gerade to ungerade and vice versa, the dominant parent state(s) can be specified as being triplet ungerade in character, either $^3\Sigma_u^\text{−}$ or $^5\Pi_u$. It is interesting to note that the former possibility leading to O($^1\text{S}$) parallels the one involved in Schumann-Runge absorption leading to O($^1\text{D}$) production, mentioned earlier in section I.

By using the RKE distribution obtained from TOF spectra at 30 eV in order to exclude the fast fragments, it was possible to construct a qualitative potential energy curve for the parent O₂ state responsible for the dominant feature at 42 μs. The result is shown in figure 7.12 assuming that the undetected fragment was O($^3\text{P}$). This curve crosses the outer edge of the Franck-Condon region close to 15 eV, and so is in reasonable agreement with the threshold measurement (figure 7.9a).
Figure 7.12  Potential energy diagram for a few of the lower lying states of O₂ showing the approximate position of the repulsive curve (dashed) responsible for O(¹S) production in this present work. The solid lines are taken from the theoretical calculations mentioned in the text, and the experimentally derived curves presented by Gilmore (1965). The Franck-Condon region for excitation from the ground state is indicated.
Extensive calculations for the valence states of $\text{O}_2$ are available in the literature (Guberman and Guisti-Suzor, 1991; Gilmore, 1965; Saxon and Liu, 1977; Guberman, 1983). Representatives of these are shown in Figure 7.12. The curve calculated from the RKE spectrum at 30 eV incident energy lies almost 4 eV below those for the optically accessible states $3^3\Sigma_u^-$ and $5^3\Pi_u$ (the latter is not shown in figure 7.12 since it is very close to the former, as is the $4^3\Sigma_g^-$ state). This is well outside error limits of both the calculations and the measurement. It is likely that the faster fragments which appear between 20 and 40 $\mu$s arise from those two parent states since there is qualitative agreement with the released kinetic energy calculated from the theoretical curves. The curve derived from the primary structure at 42 $\mu$s is near the $5^3\Pi_g$ state and this seems the most likely triplet candidate for the parent state even though it requires an optically forbidden gerade to gerade transition from the ground state. It is possible that the differences between this experimentally derived curve and the one calculated for $5^3\Pi_g$ state are due to possible thermalization delays in the Xe matrix. If a delay of a few microseconds occurred between arrival of $\text{O}(^1\text{S})$ at the Xe surface and photon emission, this could explain the approximately 1 eV shift between the experimental curve and the calculated one. Higher kinetic energy fragments would require a longer time to thermalize, hence the 1 eV gap widens at smaller internuclear separations.

Processes involving more highly excited oxygen partners such as $3s\ ^3\text{S}^o$, $3d\ ^3\text{D}^o$ or $3s'\ ^3\text{D}^o$ may make some contribution to $\text{O}(^1\text{S})$ excitation at higher electron energies. All of these are excited with relatively large cross-sections (Zipf, 1984)
following electron impact on O₂ but are unlikely to be important in the threshold region because they require incident electron energies in excess of 20 eV. Some cascade at 121.8 nm from O(3s⁺ ¹P⁰) leading to O(³S) excitation has been observed following electron impact on O₂ by James et al. (1988).

Figure 7.12 also shows the ¹Σ⁺ₚ curve leading to O(¹D) and O(³S) fragments (Guberman and Guisti-Suzor, 1991). This crosses the Franck-Condon region at lower energy than any of the triplet curves based on O(³P) + O(³S). If some excitation of this state was occurring via a spin-forbidden process, it would be observed with a threshold of less then 13 eV. In addition the sharply peaked (with energy) nature of the excitation function of such a singlet state should produce some observable perturbation to the measured excitation function in the near threshold region. Such a threshold or perturbation was not observed.
Chapter 8

The Results Obtained from Carbon Dioxide

I. Review of Earlier Work

$\text{CO}_2$ is a linear molecule with C-O bond lengths of 1.162 Å, and an ionization potential of 13.77 eV. In the dissociation limit, $\text{CO}(X^1\Sigma^+)$ and $\text{O}^3\Pi$ lie 5.45 eV above the ground vibrational state of $\text{CO}_2(X^1\Sigma^+_g)$. However, the ground state correlates adiabatically to $\text{CO}(X)$ and $\text{O}^3\Pi$ (Herzberg, 1967).

$\text{CO}_2$ was one of the molecules studied in the early EID TOF experiments (Freund and Klemperer, 1967; Clampitt and Newton, 1969). Freund (1971a) and Wells et al. (1972) resolved discrepancies between the two previous reports. Freund's TOF spectra (figure 8.1a) shows a slow fragment with a broad distribution, and a fast fragment with a sharply peaked distribution.
Figure 8.1
(a) TOF spectra from Freund (1971a) following EID of CO$_2$ at various energies.
(b) Fragment kinetic energy spectra of the O($^5$S) structure for various impact energies from the work by Misakian et al. (1975), shown as a solid line, and Alcock and McConkey (1976), shown as a dotted line. The inset is from the latter work and is an FKE distribution of O – Rydbergs produced in the dissociation. The numbers refer to production channels observed in both experiments. The slight shift in the peaks arises from inaccuracies in the conversion (see chapter 2) and are not significant.

The slow fragment was identified as CO($a^3\Pi$); the faster as O($^5$S). CO($a^3\Pi$) is responsible for the U.V. spectral features known as the Cameron bands. Freund obtained an accurate threshold of 11.80 eV for production of that fragment following EID of CO$_2$, and observed several breaks in the excitation curve as well. No assignment of the parent molecular state responsible was made, owing to the complexity of the absorption spectra in the 11–20 eV region for CO$_2$ (see, for example, Lawrence (1971), who measured the quantum yield of CO($a^3\Pi$) following
PID of CO$_2$). No analysis of the vibrational levels of CO($a^3\Pi$) in either experiment was made.

Further studies on EID of CO$_2$ were carried out concurrently by Misakian et al. (1975) and Allcock and McConkey (1976). Both of these efforts centered on the production of the fast O($^3S$) atoms. Their fragment kinetic energy spectra are shown in figure 8.1 (b). In addition to the FKE spectra, the first group reported angular distributions of O($^3S$) fragments near threshold, where anisotropies are significant, while the latter observed a notable O–Rydberg contribution to the fast peak (inset of figure 8.1b). Both groups report 5 channels contributing to the production of O($^3S$), the first of which has a threshold near 21 eV, followed by the others at 30, 43, 39, and 54 eV. Recently, Barnett et al. (1992) have also observed similar spectra. As in the case with CO production, no parent states of CO$_2$ have been assigned for production of O($^3S$).

Barnett et al. (1992) also report that the 10 eV metastable state CO($^1\Sigma^+$) (see table 2.1) is absent in TOF spectra from EID of CO$_2$, even though it is easily produced by electron impact excitation of CO (Mason and Newell, 1988). They were able to discern between the 10 eV metastable state of CO and CO($a^3\Pi$) by using detectors of different work functions. Both detectors were 7 cm from the collision region, so appreciable amounts of the 10 eV metastable state of CO would have reached them despite its 80 $\mu$s lifetime, even at thermal energies.

With regard to PID of CO$_2$, there have been no reported TOF spectra. Lawrence (1971 and 1972) has measured the quantum yield of CO($a^3\Pi$) and O($^1S$),
respectively, as a function of wavelength. The results are shown in figure 8.2 (a) and (b) respectively. The O(^1S) threshold at 128 nm in 8.2(b) is the dissociation limit of 9.64 eV, indicating a released kinetic energy of the fragments involved from about 1.0 to 4.0 eV, provided the dissociation process is solely

\[ h\nu + \text{CO}_2 \rightarrow \text{CO}_2^* \rightarrow \text{CO} \ (X^1\Sigma^+) + \text{O} (^1\Sigma) . \]  

(8.1)

Given the unity quantum yield, a possible parent state, \( \text{CO}_2^* \), might be one with the same symmetry as the ground state, i.e. \( ^1\Sigma^+ \). This would make the transition analogous to the one responsible for O(^1S) production from N\(_2\)O (see chapter 6). The complex absorption spectra of CO\(_2\) in this wavelength region does not permit a positive identification of the parent state(s) involved.

Figure 8.2  
(a) Quantum yield of CO(a^3\Pi) following PID of CO\(_2\). Thresholds of possible cascading are shown (Lawrence, 1971). (b) Quantum yield of O(^1S) following PID of CO\(_2\). The dotted portion of the curve is questionable (Lawrence, 1972).
II. Time-of-Flight and Released Kinetic Energy Spectra

After demonstrating that output signals were proportional to electron beam current and source pressure, as was shown for \( \text{N}_2\text{O} \) and \( \text{O}_2 \), TOF spectra from EID of \( \text{CO}_2 \) obtained for various electron impact energies and under conditions similar to those described in the previous two chapters were recorded and are shown on the following pages, along with their RKE transforms.

However, unlike the TOF spectra from the previous two target gases there is a very interesting difference. TOF spectra obtained with the red emissions are shown in figure 8.3. Figure 8.5 shows TOF spectra taken with the U.V. filter in place. Clearly they are distinctly different. The structure seen below 100 \( \mu \text{s} \) in figure 8.3 is still present in figure 8.5, but there it appears as a shoulder to a much brighter and broader signal spanning 100 to 400 \( \mu \text{s} \), peaking at about 180 \( \mu \text{s} \). Further examination with the monochromator (figure 8.7) revealed that this slow broad feature came from the impact of a metastable fragment on the Xe layer that produced emissions which appear to peak at 325 nm. This may not be the real maximum since the transmission of the monochromator decreases as its 300 nm lower limit is reached. The monochromator also revealed that the TOF feature between 50 and 150 \( \mu \text{s} \) had the same structure when viewed at 375 nm, or 725 nm.

From these observations, and on the basis of the previous results using \( \text{N}_2\text{O} \) and \( \text{O}_2 \) targets, it is concluded that the fast structures are due to the arrival of \( \text{O}^{(1}\text{S}) \) metastable atoms at the Xe layer. This conclusion is also based on the same
Figure 8.3 Time-of-flight spectra for O(3S) fragments produced from electron impact dissociation of CO$_2$ at various incident electron energies indicated. In each case the line drawn below each spectrum represents the baseline from which the background can be determined. The red filter (LG-595) was in place. In each case the vertical scales are not comparable. The labels are for the different dissociation channels (see text).
Figure 8.4 Released kinetic energy spectra obtained from the data of figure 8.3. These spectra have been normalized to unity at their maxima. The labels refer to the different dissociation channels shown in figure 8.3. Channel 1 appears at RKE > 5 eV, but is indistinguishable from the background.
Figure 8.5  Time-of-flight spectra for CO(a^1II) fragments produced from electron impact dissociation of CO$_2$ at various incident electron energies indicated. In each case the line drawn below each spectrum represents the baseline from which the background can be determined. The U.V. filter (UG-11) was in place. In each case the vertical scales are not comparable. The shoulder between 50 and 100 µs comes from the U.V. emission which follows the arrival of O(\(^3\)S) atoms at the Xe layer. Each spectrum was normalized to unity at its maximum.
Figure 8.6  Fragment kinetic energy spectra obtained from the data of figure 8.5. The spectra have been normalized to unity at their maxima.
Figure 8.7 Low resolution optical spectra of the emissions from the Xe layer in the 50 to 500 µs range following EID of CO₂. The features at 375 and 725 nm are due to the arrival of O(3S) atoms in the 50 to 150 µs range (figure 8.3) and the feature at 325 nm is from the arrival of CO(a3Π) fragments in the 100 to 400 µs range (figure 8.5).

arguments used in the previous two chapters. It has already been demonstrated that the detector is insensitive to O(3S) and O(1D). O(3P) would not have adequate energy to produce the emissions at the fragment kinetic energies observed.

The TOF spectra recorded in figure 8.3 are unlike those for O–Rydbergs, or CO(a3Π) fragments. Metastable C atoms could not be responsible because adiabatic separation of all the components of CO₂ in their ground state requires 17 eV (Herzberg, 1967) and as shown in the next section, the threshold lies well below that value.

The TOF spectra for O(3S) atoms in figure 8.3 appear to indicate four production channels. They will be referred to in order of appearance on the time
scale as 1, 2, 3, and 4. Channel 1 produces a very fast fragment with weak intensity in the 30-50 μs range. It appears in the 50 eV TOF spectrum and upwards. A strong channel 2 produces the narrow distribution centered at 63 μs. It makes its appearance at electron impact energies around 20 eV. This second channel is responsible for the broad feature around 2.3 eV in the corresponding RKE spectra. The third and fourth possible channels appear to be centered at 85 μs and 105 μs and correspond to released kinetic energies of 1.27 and 0.83 eV respectively. Since both channels 3 and 4 appear in the 20 eV spectrum as one broad structure, it is possible that they really are only one channel, which produces a flat topped TOF distribution.

The fragment responsible for the slow feature has been identified, by a process of elimination, and by comparison with the results of Freund (1971a) (figure 8.1a), as CO(a^3Π). This means that CO(a^3Π) fragments impinging on the Xe layer are producing U.V. emissions below 350 nm in a time which is short compared to their time-of-flight. The detection of CO(a^3Π) metastables with the use of a Xe layer is a very interesting result, and it has not been reported previously. There is clearly a shortening of the 9 ms lifetime of free CO(a^3Π) and there are no other reports in the literature of such lifetime shortening of that state by Xe. The photolysis experiments of Lawrence (1971) used He as a buffer gas.
III. Appearance Potentials and Calibrated Excitation Functions.

(1) \( \text{O}^1S \) from \( \text{CO}_2 \)

A threshold excitation curve taken with the red emissions is shown in figure 8.8. The energy scale was calibrated by observing the threshold for the prompt photons using the same method described in chapter 6. A spectrum of the prompt photon signal produced by the electron impact excitation of various states is shown in figure 8.9, for an energy of 100 eV. The prominent features are the \( \text{CO}_2^+ (A^2\Pi_u \rightarrow X^2\Pi_g) \) bands in the 300 to 480 nm range, the \( \text{CO}_2^+ (B^2\Sigma_u^+ \rightarrow X^2\Pi_g) \) bands at 288.3 and 289.6 nm (unresolved in figure 8.9), and the \( ^5P \rightarrow \text{S} \) (\( \lambda = 777.4 \) nm) and \( ^3P \rightarrow \text{S} \) (\( \lambda = 844.7 \) nm) transitions of atomic oxygen arising from dissociative excitation. Absolute cross sections for the production of the A-X and B-X emissions of the \( \text{CO}_2 \) ion following electron impact on \( \text{CO}_2 \) have been reported previously by Ajello (1971). Note that the bands at 289 nm in figure 8.9 are strongly attenuated by the transmission function of the monochromator. In reality they exceed the brightest \( \text{CO}_2^+ (A^2\Pi_u \rightarrow X^2\Pi_g) \) transition by a factor of 5.

It was assumed that calibration of the energy scale could take place by observing the threshold of the \( \text{CO}_2^+ (B^2\Sigma_u^+ \rightarrow X^2\Pi_g) \) bands at 18.3 eV with the U.V. filter (UG-11) in place. However, this placed the threshold for \( \text{O}^1S \) metastable production at a value which is too high for the lowest energies indicated in the RKE spectra if the dissociation process is
Figure 8.8  Threshold excitation function for O(1S) following EID of CO₂ using the red emissions from the Xe layer. Also shown is the threshold for the prompt photon emissions taken with the U.V. filter (UG-11) in place.

Figure 8.9  Spectrum of prompt photon emissions following 100 eV electron impact on CO₂. The resolution is 1 nm. The vertical scale has not been corrected for the variation in detection efficiency with wavelength. Note the factor of 5 magnification applied above 500 nm.
\[ e + CO_2 \rightarrow e' + CO_2^* \rightarrow e' + CO(X^1\Sigma^-) + O(^1S) \]  

(8.2)

and too low if the undetected CO fragment were in its lowest excited state.

The break in the slope of the prompt photon emission curve in figure 8.9 suggests that there is another process contributing to the prompt photon production at low energies in the spectral range transmitted by the U.V. filter. Such features have not been reported in the excitation curves for either the CO\(^2\Pi_u\) \(\rightarrow X^2\Pi_g\) or CO\(^2\Sigma_u^+\) \(\rightarrow X^2\Pi_g\) bands. It is possible that significant amounts of CO(b\(^3\Sigma^+\)) are produced from dissociative excitation of CO\(_2\) near threshold. These states cascade to the CO(a\(^3\Pi\)) state, producing the well known 3rd positive and 5B bands of CO (Pearse and Gaydon, 1963) that span the transmission range of the U.V. filter. Thus, the CO(b\(^3\Sigma^+\)) fragments would contribute to the CO(a\(^3\Pi\)) recorded in the TOF spectra of figure 8.5, and have the same released kinetic energies.

The threshold for the process

\[ e + CO_2 \rightarrow e' + CO_2^* \rightarrow e' + CO(b^3\Sigma^+) + O(^3P) \]  

(8.3)

would be about 16.0 eV, assuming the CO(b\(^3\Sigma^+\)) fragments have the same kinetic energy as the CO(a\(^3\Pi\)) fragments. This puts the threshold for the production of O(^1S) from EID of CO\(_2\) at about 11.0 eV, which is consistent with process (8.2) and the RKE data.

It was not possible to verify the presence of the most prominent transitions in the 3rd positive and 5B bands because they are below the transmission range of the available monochromator. The weaker transitions above 300 nm are probably
observable, but difficult to separate from the A-X transitions of the CO$_2$ ion due to the inadequate resolution of the monochromator.

It was expected that breaks in the excitation curve would be observed because of the three most apparent channels (2, 3, & 4) for O($^1$S) production in the TOF spectra. Such breaks are usually easy to see (e.g. as in the case of O($^2$S) from EID of CO$_2$, Allcock and McConkey, 1976). Their absence in figure 8.8 might be explained if the thresholds for each channel are rather shallow or too broad to be resolved by the electron gun, or, if pre-dissociation is taking place.

An excitation curve for O($^1$S) production from threshold to 1000 eV is shown in figure 8.10. The vertical scale was calibrated by comparison with O($^1$S) production.

![Calibrated excitation curve for O($^1$S) production following EID of CO$_2$ for electron impact energies from 0 to 1000 eV.](image-url)
from N₂O at 100 eV, as described in the last chapter. This time, the calibration was made easier since N₂O and CO₂ have the same mass and so their densities in the interaction region should be the same for identical source pressures. By recording all O(^1S) produced by EID of CO₂ and then alternating to N₂O, and then back to CO₂, etc., for the same source pressures, it was found that the ratio of O(^1S) production from CO₂ to that from N₂O was 0.77 ± 0.04 at 100 eV, after normalizing for current and assuming identical attenuation coefficients. This result is σ = 1.45 ± 0.15 \times 10^{-17} \text{ cm}^2 for O(^1S) production from EID of CO₂. The uncertainty includes the 10% uncertainty for the cross section from N₂O. The rest of the 0–1000 eV excitation curve was normalized to this value, and the results tabulated in table 8.1 following the drawing a smooth curve fitted by eye through the data of figure 8.10.

The excitation curve shows a rise to a broad maximum at 50 eV and a fall off at higher energies according to ln(E)/E. Thus, an optically allowed transition appears to be the dominant production mechanism for O(^1S) from CO₂. If this channel is described by (8.2), then a likely candidate for the parent dissociating state is CO₂(^1Σ^+). The transition would be identical to the one which produces O(^1S) from EID of N₂O (chapter 6). If this is the case, then, as with N₂O, the angular distribution of fragments would be isotropic at all electron impact energies in accordance with Dunn's rules (Dunn, 1962).

By fitting the data from figure 8.10 to the Bethe-Born approximation, equation (3.15), at energies over 500 eV, and using a transition energy of 10.4 ± 0.5 eV, it was possible to calculate the optical dipole oscillator strength, f_n,
and the constant $C_n$, for the transition. The results were $f_n = 0.35 \pm 0.04$ and $C_n = 0.040 \pm 0.001$ respectively.

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Table 8.1 Integral cross sections for the production of $O(^1S)$ following electron impact dissociation of $CO_2$. 
(2), CO(a^3\Pi) from CO_2

The threshold excitation curve for production of CO(a^3\Pi) following EID of CO_2 is shown in figure 8.11 (a), along with the production curve for prompt photons. Below that, figure 8.11 (b), is the same curve spanning electron impact energies from threshold to 1000 eV.

There is a possible feature at 17 eV in figure 8.11 (a). It may be due to cascading from the CO(b^3Sigma^+) state, but the data is inconclusive. The break labelled B1 at 21 eV could possibly be the result of the process

\[ e + CO_2 \rightarrow e' + CO_2^* \rightarrow e'' + CO(b^3Sigma^+) + O(^1S) \]

which has a threshold at 20.1 eV. However, such a break was not observed in the excitation function for O(^1S) in figure 8.8. It is possible that the new channel arises from production of CO(a^3\Pi) and O(^5S), which has a threshold at 21 eV, measured by Allcock and McConkey (1976) and Misakian et al. (1975).

The relative excitation function for CO(a^3\Pi) following EID of CO_2 from threshold to 1000 eV was calibrated by using the integral cross section for this process measured by Erdman and Zipf (1983). They reported a large value of \(2.4 \times 10^{-16} \text{ cm}^2\) at 80 eV. The results are tabulated in table 8.2.

It was not possible to calculate the quantum efficiency of the Xe layer for detection of CO(a^3\Pi) fragments because the spectrum of photons emitted following their arrival at the Xe layer could be partly outside the transmission range of the monochromator (300-850 nm). This spectral information is necessary in order to
Figure 8.11  (a) Excitation function for CO(a^2II) produced by EID of CO₂ near threshold. The prompt photon result is also shown. The break labelled B1 is discussed in the text.  
(b) Excitation function for the same fragment from threshold to 1000 eV.
correct for the transmission and detection efficiencies of the U.V. filter - photomultiplier combination. In addition, the fraction of CO(a^3Π) scattered or quenched en route to the detector by collisions with the background gas is unknown.

Given the large cross section for the process, the signal intensity of CO(a^3Π) fragments is much lower than anticipated. Thus, either the Xe layer is much less efficient at detecting CO(a^3Π) than it is for O(^1S) (for the latter process, an estimate of 25% was obtained in chapter 5), or, much of the emission from the interaction of CO(a^3Π) with the Xe surface is not transmitted to the photomultiplier. Since the lifetime for CO(a^3Π) is approximately 9 ms (Erdman and Zipf, 1983), only about 5% of them will decay before reaching the Xe layer.

Table 8.2 Integral cross sections for the production of CO(a^3Π) following electron impact dissociation of CO₂.

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Chapter 9

Conclusions

The Xe layer detector described in this paper has been demonstrated to be selectively sensitive to the metastable atom O(^1S). It is also sensitive to CO(a^3Π), but discrimination between these species is easily accomplished by a suitable choice of filter, since the species produce significantly different emissions after impact on the Xe layer. This detection method has been successfully used to study the electron impact dissociation of N_2O, O_2, and CO_2 using TOF techniques. Rather simple TOF spectra are obtained. The absolute cross-sections for production of O(^1S) from all parent molecules has been established.

The cross section data from this work for O(^1S) production from electron impact dissociation of O_2 is plotted in figure 9.1, along with the recommended data for O(^1S) production by electron impact excitation of O (Lahe and Gilmore, 1990).
Figure 9.1 Comparison of cross section data for production of O(1S) from atomic and molecular parents. The O₂ data are the measurements this work while the O data are from Lahee and Gilmore (1990). A representative error bar is included on the O₂ data.

The cross section for O₂ is observed to rise quite steeply from threshold reaching half its maximum value by the time the incident energy has reached 25 eV, i.e. approximately 10 eV above threshold. Clearly the cross-section for production of O(1S) from O(3P) dominates at the lower electron energies (≤ 10 eV) where the maximum in auroral electron intensities lie (Rees, 1989). However even at say 20 eV where auroral electron intensities have fallen off by an order of magnitude from their value at 10 eV, the cross-sections for producing O(1S) via the two channels differ by less than a factor of three. Thus at altitudes around 100 km and below where O₂ molecular number densities are 10 times or more higher than O-atom densities, (see
figure 9.2) electron impact on $O_2$ could be a significant production mechanism of $O(^{1}S)$ in aurora. A complete assessment is beyond the scope of this thesis, but the data obtained from this work is certainly of value to modellers of the aurora (McConnell, 1993).

![Graph showing the number densities of O and O$_2$ as a function of altitude.](image)

**Figure 9.2** Number densities for O and O$_2$ as a function of altitude (Rees, 1989).
There are several obvious suggestions for improving the experiment. It is hoped that sufficient funds will become available to further develop the apparatus. One important improvement would be with regard to the collection of light emitted from the Xe layer (a simple lens did not increase the signal significantly; in fact it increased the background as well, and so was never used). A better means of regulating the cold finger temperature should be devised. The addition of a cryostat capable of lower temperatures would be a very welcome, but expensive addition. Using a fast multi-channel scalar instead of the time-to-amplitude convertor would eliminate dead time effects. A modification enabling angular distribution of the fragments to be measured should be done to check the assumption that they were emitted isotropically. A photomultiplier with a higher infrared response and some other detector for V.U.V. emissions might reveal interesting results.

There are many possibilities with this metastable conversion technique. Plans are underway to study more oxygen containing molecules (e.g. CO and NO) using the Xe surface. Other surfaces will be tried as well, such as solid argon (if a liquid He cryostat becomes available) or porphyrin molecules. The latter are known to be sensitive to $\text{O}_2(a^1\Delta_g)$ (Rochkind and Ouaknine, 1992) which produces one of the brightest airglow emissions.
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**Vita Auctoris**

Lance Richard LeClair was born on December 14, 1963, in Clinton, Ontario, but lived in Dalhousie, New Brunswick, for the next 20 years. He graduated from Dalhousie Regional High School in 1981. After a year away from school, he enrolled at Mt. Allison University in Sackville, N.B., and graduated with honours in 1986 with a B.Sc. in Physics. He was awarded an NSERC post graduate scholarship to continue studies at the University of Western Ontario, and obtained an M.Sc. in Physics from that institution in 1989. He then enrolled at the University of Windsor, and attained the degree of Ph.D. in 1993.