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Geoffrey. Allcock

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THE STUDY OF MOLECULAR DISSOCIATION BY
TIME-OF-FLIGHT SPECTROSCOPY

by

GEOFFREY ALLCOCK

A Thesis
Submitted to the Faculty of Graduate Studies through the
Department of Physics in Partial Fulfillment
of the Requirements for the Degree of
Master of Science at the
University of Windsor

Windsor, Ontario

1975
TO MY WIFE AND PARENTS

Trust in the Lord with all thine heart;
and lean not unto thine own understanding.

Proverbs 3:5.
ABSTRACT

An apparatus has been developed in order to study the metastable fragments produced during the dissociation of simple molecules. These molecules are excited by electron impact and the metastable fragments are studied by Time-of-Flight Spectroscopy. Results are presented for the fast metastable fragments produced during the dissociation of N₂, CO₂ and N₂O. Four principal features were observed in the N₂⁺ time-of-flight spectra and in the corresponding kinetic energy distributions. The calculated dissociation limits of the molecular parent states which result in the production of these fragments correspond to the dissociation limits of a number of N₂⁺ states. This observation suggests that the excitation involves the production of high-Rydberg molecules and that atoms in high-Rydberg states are produced during the dissociation of these molecules. The core-ion model for this dissociation process is discussed and the fragment states are identified.

Studies of the fast fragments produced during the dissociation of CO₂ have revealed the participation of two distinct processes which involve the production of \(^5\)S⁰ oxygen atoms. It is likely that one of these processes involves a cascade mechanism. Of the two remaining processes, it is likely that at least one involves the production of a high-Rydberg oxygen atom.

Preliminary results for the fast metastable fragments produced during the dissociation of N₂O are also presented.
ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the constant guidance and supervision of Dr. J.W. McConkey throughout the entire course of this work. I would also like to thank Dr. J. Fryar and Mr. K-H. Tan for a number of helpful discussions and suggestions. Special thanks are also due to the technical staff of the Department and to Mr. Jack Eisenberg for providing the computer software. I am also indebted to Mrs. Jean Franklin for typing the manuscript.

Finally, it is with deep gratitude that I acknowledge the continual support and encouragement of my wife, Marilyn.

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# Table of Contents

<table>
<thead>
<tr>
<th>Chapter/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>LIST OF TABLES</td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>x</td>
</tr>
<tr>
<td>INTRODUCTION AND MOTIVATION FOR RESEARCH</td>
<td>1</td>
</tr>
<tr>
<td>CHAPTER 1</td>
<td></td>
</tr>
<tr>
<td>Theoretical Considerations</td>
<td>5</td>
</tr>
<tr>
<td>1.1 The Franck-Condon Principle</td>
<td>6</td>
</tr>
<tr>
<td>1.2 Dissociation Energetics</td>
<td>9</td>
</tr>
<tr>
<td>1.3 The Importance of Excitation Functions in the Study of Metastable Atoms and Molecules</td>
<td>11</td>
</tr>
<tr>
<td>1.3.1 The General Shape of Excitation Functions</td>
<td>11</td>
</tr>
<tr>
<td>1.3.2 The Detailed Structure of Excitation Functions</td>
<td>13</td>
</tr>
<tr>
<td>1.4 Symmetry Considerations in Molecular Dissociation</td>
<td>15</td>
</tr>
<tr>
<td>1.5 The Angular Distribution of Dissociation Fragments</td>
<td>18</td>
</tr>
<tr>
<td>1.6 Fragment Kinetic Energy Shifts due to Momentum Transfer</td>
<td>24</td>
</tr>
<tr>
<td>CHAPTER 2</td>
<td></td>
</tr>
<tr>
<td>A Review of Some Experimental Approaches to Metastable Excitation and Detection</td>
<td>26</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>27</td>
</tr>
<tr>
<td>2.2 Direct and Indirect Detection of Metastable Atoms and Molecules</td>
<td>27</td>
</tr>
<tr>
<td>2.3 A Review of Some Experiments which Utilize Different Techniques of Metastable Excitation and Detection</td>
<td>28</td>
</tr>
<tr>
<td>2.3.1 Direct Detection Following Excitation by Electron Impact</td>
<td>28</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>2.3.2 Indirect Detection Following Excitation by Electron Impact</td>
<td>30</td>
</tr>
<tr>
<td>2.3.3 Direct Detection Following Excitation by Photon Absorption</td>
<td>31</td>
</tr>
<tr>
<td>2.3.4 Indirect Detection Following Molecular Excitation by Photon Absorption</td>
<td>34</td>
</tr>
<tr>
<td><strong>CHAPTER 3</strong></td>
<td></td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>37</td>
</tr>
<tr>
<td>3.2 A Review of the Experiment</td>
<td>37</td>
</tr>
<tr>
<td>3.3 Description of the Apparatus</td>
<td>40</td>
</tr>
<tr>
<td>3.3.1 The Vacuum System</td>
<td>40</td>
</tr>
<tr>
<td>3.3.2 The Electron Gun</td>
<td>42</td>
</tr>
<tr>
<td>3.3.3 The Detector System</td>
<td>44</td>
</tr>
<tr>
<td>3.4 The Apparatus Electronics and Data Accumulation Systems</td>
<td>47</td>
</tr>
<tr>
<td>3.4.1 The Electron Gun Pulsing Mode</td>
<td>47</td>
</tr>
<tr>
<td>3.4.2 Manual Time-of-Flight Data Accumulation</td>
<td>48</td>
</tr>
<tr>
<td>3.4.3 Time-of-Flight Data Accumulation by Pulse Height Analyser</td>
<td>49</td>
</tr>
<tr>
<td>3.4.4 Time-of-Flight Data Accumulation by Computer</td>
<td>50</td>
</tr>
<tr>
<td>3.4.5 Excitation Function Data Accumulation</td>
<td>53</td>
</tr>
<tr>
<td>3.5 Apparatus Performance and Special Experimental Techniques</td>
<td>54</td>
</tr>
<tr>
<td>3.5.1 The Electron Gun Performance</td>
<td>54</td>
</tr>
<tr>
<td>3.5.2 Preparation of the Low Work-Function Detector and General Detector Performance</td>
<td>60</td>
</tr>
<tr>
<td>3.6 Degradation of the Time-of-Flight and Kinetic Energy Resolutions</td>
<td>62</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>3.7  Experimental Uncertainties - The Nett</td>
<td>65</td>
</tr>
<tr>
<td>EFFECT</td>
<td></td>
</tr>
<tr>
<td>CHAPTER 4 THE RESULTS FOR NITROGEN</td>
<td>67</td>
</tr>
<tr>
<td>4.1  Introduction</td>
<td>68</td>
</tr>
<tr>
<td>4.2  Description of the N⁺ Results</td>
<td>68</td>
</tr>
<tr>
<td>4.2.1 N⁺ Signal Intensity as a Function of</td>
<td>58</td>
</tr>
<tr>
<td>Gas Pressure and Electron Current</td>
<td></td>
</tr>
<tr>
<td>4.2.2 Time-of-Flight and Kinetic Energy</td>
<td>70</td>
</tr>
<tr>
<td>Distributions of N⁺</td>
<td></td>
</tr>
<tr>
<td>4.2.3 Photon Contamination of the N⁺ Time-</td>
<td>74</td>
</tr>
<tr>
<td>of-Flight Distributions</td>
<td></td>
</tr>
<tr>
<td>4.2.4 N⁺ Excitation Functions</td>
<td>78</td>
</tr>
<tr>
<td>4.3  Discussion of the N⁺ Results</td>
<td>78</td>
</tr>
<tr>
<td>4.4  Comparison of the N⁺ Results with</td>
<td>86</td>
</tr>
<tr>
<td>Published Data</td>
<td></td>
</tr>
<tr>
<td>CHAPTER 5 THE RESULTS FOR CARBON DIOXIDE</td>
<td>90</td>
</tr>
<tr>
<td>5.1  Introduction</td>
<td>91</td>
</tr>
<tr>
<td>5.2  Description of the Fast Fragment Results</td>
<td>91</td>
</tr>
<tr>
<td>5.2.1 Signal Intensity of the Fast Fragments</td>
<td>91</td>
</tr>
<tr>
<td>as a Function of Gas Pressure and Electron</td>
<td></td>
</tr>
<tr>
<td>Current</td>
<td></td>
</tr>
<tr>
<td>5.2.2 Time-of-Flight and Kinetic Energy</td>
<td>92</td>
</tr>
<tr>
<td>Distributions of the Fast Fragments</td>
<td></td>
</tr>
<tr>
<td>5.2.3 The Fast Fragment Excitation Functions</td>
<td>94</td>
</tr>
<tr>
<td>5.3  Discussion of the Fast Fragment Results</td>
<td>96</td>
</tr>
<tr>
<td>5.4  Comparison of the Fast Fragment Results</td>
<td>104</td>
</tr>
<tr>
<td>with the Results of Other Workers</td>
<td></td>
</tr>
<tr>
<td>CHAPTER 6 THE RESULTS FOR NITROUS OXIDE</td>
<td>107</td>
</tr>
<tr>
<td>6.1  Introduction</td>
<td>108</td>
</tr>
</tbody>
</table>
6.2 Description of the Fast Fragment Results
   6.2.1 The Signal Intensity of the Fast Fragments as a Function of Gas Pressure and Electron Current
   6.2.2 Time-of-Flight Distributions of the Fast Fragments
   6.2.3 Discussion and Comparison of the Fast Fragment Results

CHAPTER 7 CONCLUSIONS
   7.1 Summary and Conclusions
   7.2 Future Developments

APPENDIX 1
APPENDIX 2
APPENDIX 3
BIBLIOGRAPHY
VITA AUCTORIS
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dunn's transition probabilities for the excitation of homonuclear molecules</td>
<td>17</td>
</tr>
<tr>
<td>2</td>
<td>Dunn's transition probabilities for the excitation of heteronuclear molecules</td>
<td>17</td>
</tr>
<tr>
<td>3</td>
<td>The results for nitrogen - a comparison of the measured dissociation limits with the dissociation limits of a number of N₂ states.</td>
<td>81</td>
</tr>
<tr>
<td>4</td>
<td>The results for Carbon Dioxide - a comparison of the measured dissociation limits with the dissociation limits of a number of possible processes.</td>
<td>99</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>1.</td>
<td>Electronic transitions in molecules - three possible consequences of the Franck-Condon principle.</td>
<td>7</td>
</tr>
<tr>
<td>2.</td>
<td>Two possible kinetic energy distributions of dissociation fragments.</td>
<td>7</td>
</tr>
<tr>
<td>3.</td>
<td>The momentum transfer vector and its relation to the momentum of the incident electron and the momentum of the scattered electron</td>
<td>19</td>
</tr>
<tr>
<td>4.</td>
<td>Theoretical angular distributions of 4.38 eV protons produced during the electron impact dissociation of H₂⁺</td>
<td>19</td>
</tr>
<tr>
<td>5.</td>
<td>A typical time-of-flight apparatus which features the direct detection of metastable fragments following excitation by electron impact.</td>
<td>29</td>
</tr>
<tr>
<td>6.</td>
<td>An apparatus featuring the indirect detection of metastable fragments following excitation by electron impact.</td>
<td>29</td>
</tr>
<tr>
<td>7.</td>
<td>A Photofragment Spectrometer which features the direct detection of dissociation fragments following excitation by photon absorption.</td>
<td>33</td>
</tr>
<tr>
<td>8.</td>
<td>A side view of the Photofragment Spectrometer showing its associated laser system.</td>
<td>33</td>
</tr>
<tr>
<td>9.</td>
<td>An apparatus featuring the indirect detection of metastable fragments following excitation by photon absorption.</td>
<td>35</td>
</tr>
<tr>
<td>10.</td>
<td>A typical time-of-flight spectrum.</td>
<td>39</td>
</tr>
<tr>
<td>11.</td>
<td>The vacuum system.</td>
<td>41</td>
</tr>
<tr>
<td>12.</td>
<td>The electron gun.</td>
<td>43</td>
</tr>
<tr>
<td>13.</td>
<td>The double detector system.</td>
<td>45</td>
</tr>
<tr>
<td>14.</td>
<td>The electron gun circuit.</td>
<td>43</td>
</tr>
<tr>
<td>15.</td>
<td>Three modes of automatic data accumulation.</td>
<td>51</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>----------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>16.</td>
<td>The collector current as a function of collector voltage.</td>
<td></td>
</tr>
<tr>
<td>17.</td>
<td>The current on the outer collector as a function of electron energy.</td>
<td></td>
</tr>
<tr>
<td>18.</td>
<td>The electron pulse profile at two different width settings.</td>
<td></td>
</tr>
<tr>
<td>19.</td>
<td>A typical He* excitation function.</td>
<td></td>
</tr>
<tr>
<td>20.</td>
<td>Fragment signal intensity as a function of gas pressure for Nitrogen, Carbon Dioxide and Nitrous Oxide.</td>
<td></td>
</tr>
<tr>
<td>21.</td>
<td>Fragment signal intensity as a function of electron current for Nitrogen, Carbon Dioxide and Nitrous Oxide.</td>
<td></td>
</tr>
<tr>
<td>22.</td>
<td>The N* time-of-flight spectra.</td>
<td></td>
</tr>
<tr>
<td>23.</td>
<td>N* signal intensity as a function of the total kinetic energy released during dissociation.</td>
<td></td>
</tr>
<tr>
<td>24.</td>
<td>An excitation function for the photons observed in the N* time-of-flight spectra.</td>
<td></td>
</tr>
<tr>
<td>25.</td>
<td>A comparison of the theoretical and observed photon decay curves.</td>
<td></td>
</tr>
<tr>
<td>26.</td>
<td>The present N* excitation functions and the excitation functions obtained by Smyth and Freund.</td>
<td></td>
</tr>
<tr>
<td>27.</td>
<td>Comparison of the present N* results with the N+ results of Kieffer and Van Brunt.</td>
<td></td>
</tr>
<tr>
<td>28.</td>
<td>Comparison of the present N* results with the N* results of Smyth and Freund.</td>
<td></td>
</tr>
<tr>
<td>29.</td>
<td>The N* time-of-flight spectra obtained by Smyth and Freund.</td>
<td></td>
</tr>
<tr>
<td>30.</td>
<td>Time-of-flight spectra of the fast fragments produced during the dissociation of Carbon Dioxide.</td>
<td></td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>31.</td>
<td>Kinetic energy distributions of the fast fragments produced during the dissociation of Carbon Dioxide.</td>
<td>95</td>
</tr>
<tr>
<td>32.</td>
<td>Excitation functions of the fast fragments produced during the dissociation of Carbon Dioxide.</td>
<td>97</td>
</tr>
<tr>
<td>33.</td>
<td>Comparison of the present Carbon Dioxide results with the results of Misakian and Mumma.</td>
<td>105</td>
</tr>
<tr>
<td>34.</td>
<td>Time-of-Flight spectra of the fast fragments produced during the dissociation of Nitrous Oxide.</td>
<td>110</td>
</tr>
<tr>
<td>35.</td>
<td>A time-of-flight spectrum of the fragments produced during the dissociation of Nitrous Oxide at low electron energy.</td>
<td>112</td>
</tr>
<tr>
<td>36.</td>
<td>The time-of-flight slit function obtained by convoluting a rectangular electron pulse with a rectangular time-of-flight window.</td>
<td>119</td>
</tr>
<tr>
<td>37.</td>
<td>Photon signal lasses due to molecular diffusion - the effect of the present apparatus geometry.</td>
<td>123</td>
</tr>
</tbody>
</table>
INTRODUCTION AND MOTIVATION FOR RESEARCH
Excited atoms and molecules with long lifetimes can be extensively studied by Time-of-Flight Spectroscopy following excitation by electron or photon impact. This technique involves the measurement of translational kinetic energy distributions of fragment atoms or molecules following dissociative excitation of a parent molecule. These measurements provide information on repulsive and predissociated states of the parent molecule as well as cross sections for specific excitation processes. In addition, the availability of angular distributions allows the study of parent molecule state symmetries.

The fairly recent surge in interest in metastable atoms and molecules seems well founded as science and technology become more environmentally conscious and lasers become increasingly utilized. For example, a review of the major atomic and molecular processes taking place in the upper and middle atmosphere shows immediately the importance of certain metastable states of Oxygen and Nitrogen. In particular metastable states of atomic oxygen are the result of photodissociation of molecular oxygen in the thermosphere following the absorption of ultraviolet radiation.

\[ \text{O}_2 + h\nu(\lambda < 1759\text{Å}) \rightarrow \text{O}^{(3P)} + \text{O}^{(1D)} \]  

Schumann-Runge continuum Metastable

At lower altitudes photodissociation of ozone during stratospheric absorption of near ultraviolet radiation also yields metastable oxygen.

\[ \text{O}_3 + h\nu(\lambda < 3500\text{Å}) \rightarrow \text{O}_2^{(1\Delta)} + \text{O}^{(1D)} \]  

Hartley continuum Metastable Metastable
At higher altitudes the metastable states $O(1S)$ and $O(1D)$ in addition to the corresponding states of atomic nitrogen are produced via dissociative recombination of electrons and the molecular parents. The importance of $O(1D)$ is further emphasized by consideration of some of the major reactions which lead to the build-up and breakdown of the stratospheric ozone layer (Nicolet, 1974). For example, $O(1D)$ forms an important source of atomic oxygen for ozone production (through 3-body reactions with $O_2$ and another molecule) and, in addition, it reacts with atmospheric $H_2O$ to give the OH radical which attacks ozone.

Studies of the mechanisms involved in the production of the Earth's ozone layer have now taken on a new importance due to the threat of high altitude atmospheric pollution. In particular, fear has been expressed that increased concentrations of the oxides of nitrogen at these altitudes may upset the delicately balanced natural processes. Supersonic transporters and atmospheric nuclear tests are known to pollute the atmosphere in this way. In addition, increasing concentrations of chlorine containing compounds, such as Freon, pose a major threat to the ozone layer.

Major processes involved in the Atmospheric Airglow also involve metastable atoms and molecules. In particular, emissions from metastable states of atomic oxygen are important. These are also parent states of some of the prominent auroral emissions (Chamberlain, 1961). Metastable species are prominent in other planetary atmospheres as well. Metastable $O(1S)$ and $O(1D)$ are strongly represented in the atmospheres of Mars and Venus, being
produced by photodissociation of CO₂ and also dissociative recombination of O₂⁺ and CO₂⁺. The dayglow spectrum of Mars includes a variety of emission features of which the Cameron bands of metastable CO(a^3Π - X^1Σ⁺) are important (McConnel et al, 1970).

Population inversion in many laser systems involves metastable states and so any information regarding the production of these states is useful. For example, work is currently being undertaken on the feasibility of an oxygen atom laser using the 5577 Å line of atomic oxygen. Photodissociation of nitrous oxide and carbon dioxide has been suggested as a method of obtaining the O(1S) metastable state for this purpose (Rockwood, 1973) (Murray et al, 1973).

It is the purpose of the present work to develop an apparatus capable of directly monitoring the production of metastable species, particularly those of atmospheric, planetary and laser interest.

The difficulties involved in unambiguously and directly monitoring metastable species have led workers to the development of Time-of-Flight Spectroscopy. Metastable atoms and molecules can be directly detected by Auger electron emission from metal surfaces of sufficiently low Work Function. However, the detection of very low lying metastable states with internal energy less than 5eV requires the preparation of special surfaces. The very important atomic oxygen metastable states O(1S) and O(1D) are such low lying states. This work involves the development of techniques to detect such metastable states.
CHAPTER 1

THEORETICAL CONSIDERATIONS
1.1 *The Franck-Condon Principle*

An electron transition in a molecule can occur during electron impact, photon absorption or photon emission. The way in which the molecular nuclei behave during such a transition is summarized by the Franck-Condon principle. This principle states that, in an electron transition, the nuclear separation and velocity of relative nuclear motion alter only by a negligible amount. In other words, the transition takes place so quickly that the nuclei do not have time to move an appreciable distance. It is thus possible to predict the consequences of an electron transition by study of the potential energy curves of both the initial and final electronic states.

To illustrate this point, three possible transitions in a molecule AB are shown in Fig. 1. In all three cases the transition takes place between a ground state potential energy curve and an upper state potential energy curve. The upper state curves do, however, differ in shape and may correspond to the excited states of either a molecule or molecular ion. The nuclear separation in the ground vibrational level will effectively lie between the limits a and b in all cases. Hence, according to the Franck-Condon principle, the nuclear separation still lies between these limits after the transition. Referring to Fig. 1, the final state of the molecule will therefore be represented by points lying between c and d on the upper curves. The three cases that are illustrated thus result in the following consequences.
Fig. 1. Electronic transitions in molecules from a given initial state to three final states having different potential energy curves, illustrating the consequences of the Franck-Condon principle.

Fig. 2. Kinetic energy distribution of products of dissociation by electron impact: (a) when the final state has a potential energy curve similar to IIb of Fig. 1 (b); (b) when the final state has a potential energy curve similar to IIa of Fig. 1 (c).
Case (a) The final state always lies within the region of the discrete vibrational levels of the upper potential energy curve and thus the transition always results in a stable electronically excited molecule (or molecular ion) possessing some degree of vibrational excitation.

Case (b) The region in which the final state must lie includes some part of the continuum as well as some discrete vibrational levels. A certain proportion of the transitions will therefore lead to dissociation of the molecule (or molecular ion) while others will produce stable excited molecules (or molecular ions). During the dissociation the molecule (or molecular ion) splits into two atoms A' and B'' (or an atom and an ion) with relative kinetic energies ranging from 0 to $E_c$ as shown in Figs. 1(b) and 2(a).

Case (c) The final state always lies within the continuum of vibrational levels. In this case, dissociation of the molecule (or molecular ion) accompanies all transitions between the lower and upper electronic states. The relative kinetic energies of the atoms (or atom and ion) into which the molecule (or molecular ion) dissociates will lie between $E_d$ and $E_c$ as shown in Figs. 1(c) and 2(b).

The atoms produced during the dissociation of a molecule (or molecular ion) may either be in electronically excited states or in the ground state. This depends entirely on the dissociation limit of the particular molecular (or molecular ion) parent state. In a similar way, the dissociation limit of a
molecular ion state may correspond to the production of excited or ground state atomic ions.

Similar considerations to the above apply to downward transitions in a molecule. These transitions may also result in the production of a stable molecule or lead to molecular dissociation, depending on the nature of the potential energy curve for the lower state and the nuclear separation involved.

Some of the excited molecular states, produced by electron impact, may be metastable and the dissociation of others may result in metastable fragments.

1.2 Dissociation Energetics

Consider a transition from the ground state of a molecule AB to an upper electronic state of the molecule. Take as the zero of potential energy the energy of the ground vibrational level of the ground state. Let $D_{AB}$ be the dissociation energy of AB and $W_{\text{min}}$ the minimum energy of relative motion of the atoms $A'$ and $B''$ after the dissociation. Thus, if $U'_A$ and $U''_B$ are the excitation energies of these atoms, then according to the Franck-Condon principle, the minimum energy $E_{\text{min}}$ necessary to produce the transition is given by

$$E_{\text{min}} = U'_A + U''_B + W_{\text{min}} + D_{AB}$$

as may be seen from Fig. 1(c) in which $W_{\text{min}} = E_d$. A more general expression than the above is given by
\[ E = U_A' + U_B'' + W + D_{AB} = D_{AB}' + W \] (4)

where \( E \) is now the energy required to produce a transition anywhere within the Franck-Condon region, \( W \) is the resulting kinetic energy of the relative motion of \( A' \) and \( B'' \) and \( D_{AB}' \) is the dissociation limit of the excited molecule.

The importance of Eq. (4) lies in the fact that it may be possible to obtain information about \( D_{AB}' \) or the nature of the products \( A' \) and \( B'' \) by measuring \( E \) and \( W \). In any such measurement it is usually only possible to determine the kinetic energy of one of the fragments. However, given this information and the necessary condition of momentum conservation, it follows that

\[ W = \frac{M_{AB}}{M_A} W_B \] (5)

where \( W_B \) is the measured kinetic energy of \( B'' \), \( M_{AB} \) is the mass of the molecule and \( M_A \) is the mass of fragment \( A' \).

The kinetic energy \( W_B \) of fragment \( B'' \) can be determined by measuring the fragments transit time over a known distance. This is exactly what is done during time-of-flight spectroscopy.

In an electronic transition that can lead to dissociation, the resulting atoms may have a finite range of relative kinetic energies. It is of interest and importance to have some means of estimating the probability that a given fragment will have a particular energy in this range. This probability is a reflection of the probability that the nuclear separation should have a particular value in the classically
allowed range. Thus, referring to Fig. 1(c), the probability that a transition be from \( \ell \) to \( m \) is determined mainly by the probability that the nuclear separation of the initial state be \( R_\ell \). This probability is given by the value of \( |\chi_{no}(R_\ell)|^2 \), where \( \chi_{no} \) is the vibrational wave function of the lowest vibrational state. The distribution of this probability as a function of \( R_\ell \) is shown in Fig. 1(c). The probability reaches a single maximum at about the centre of the Franck-Condon region and falls off rapidly outside the region of classically allowed motion. Using this function as a weighting factor, the energy distributions of the atoms resulting from transitions of respective types (b) and (c) take the forms illustrated in Fig. 2. There is a characteristic difference between these two energy distributions. In the former case, illustrated in Fig. 2(a), atoms with zero kinetic energy may be produced and the curve falls off quite sharply at the low energy side, whereas in case (c), illustrated in Fig. 2(b), the atoms always have some finite kinetic energy and the curve remains nearly symmetrical.

Thus it is possible, in principle, to distinguish between the dissociation of molecules in repulsive states (such as in Fig. 1(c)) and the dissociation of molecules in bound states (such as in Fig. 1(b)).

1.3 The Importance of Excitation Functions in the Study of Metastable Atoms and Molecules

1.3.1 The General Shape of Excitation Functions

Excitation functions, which are recordings of signal
intensity against electron energy, have a characteristic high energy dependence which depends on the specific excitation mechanism being studied. In the present experiment, this signal intensity corresponds to the signal intensity of directly detected metastable atoms and molecules and its high energy dependence is a reflection of the behaviour of the cross-section for metastable excitation at high energy. If the excitation involves only optically forbidden transitions (e.g. the excitation of molecular metastable states), then according to the first Born approximation, the high energy cross-section for excitation of all these states falls off as the reciprocal of the incident electron energy $E$. However, if a study is made of the metastable fragments produced during the dissociation of optically allowed molecular states, then according to the same approximation, the high energy cross-section for production of all these fragments falls off as $E^{-1}$ in $CE$, where $C$ is a constant. Furthermore, if any of the above excitations involve electron exchange (i.e. a change of multiplicity between the initial and final states of the molecule), then according to Ochkur approximation, the high energy cross-section for excitation of that particular state falls off as $E^{-3}$. It is thus possible to directly identify specific excitation mechanisms by observation of the shape of excitation functions at high energy.

At very low electron energies (i.e. below all excitation thresholds) the cross-section for excitation is zero and at high electron energies the cross-section falls off in accordance with the Born approximation. Thus, between these
two limits, the cross-section rises and then goes through a maximum.

1.3.2 The Detailed Structure of Excitation Functions

Consider an excitation function obtained by plotting the signal intensity of metastable molecules against electron energy. If the electron energy is less than the excitation energy of the lowest molecular metastable state, then zero signal will be observed. This remains the case until the electron energy is sufficient to cause a transition from the ground state of the molecule to the first accessible vibrational level of the metastable state. At this point the first signal will be observed and it continues to increase in magnitude as the cross-section for excitation of the vibrational level increases. If the incident electron beam is sufficiently monoenergetic and high resolution detection is possible, then it may be possible to observe the excitation of different vibrational levels in the metastable molecule. The excitation of each of these levels would then cause an increase in the observed signal and hence a change in slope of the excitation function. However, poor resolution usually prevents such detailed observations and thus the total signal due to excitation of the metastable electronic state rises smoothly as the cross-section for its excitation increases. This continues until the electron energy is sufficient to excite the next molecular metastable state.
At this energy an observable change in the slope of the excitation function occurs. It is thus possible to measure the minimum energy required to excite the molecule from its ground state to each molecular metastable state (i.e. the metastable state excitation energies).

In a similar way, it is possible to measure the dissociation limit of the optically allowed states which result in metastable fragments. This is done by recording excitation functions in which only metastable fragments with a fixed range of known kinetic energies are recorded. This enables the electron energy to be measured at the first appearance of each fragment on the excitation functions. It then follows from Eq. (4) that the dissociation limit $D'_{AB}$ of each of these molecular parent states is given by

$$D'_{AB} = E_{APP} - W \tag{6}$$

where $E_{APP}$ is the electron energy at fragment appearance and $W$ is the kinetic energy of relative motion of the dissociation fragments.

It also follows from Eq. (4) that

$$D'_{AB} = U'_A + U''_B + D_{AB} \tag{7}$$

where $U'_A$ and $U''_B$ are the excitation energies of the fragments and $D_{AB}$ is the dissociation limit of the ground state of the molecule $AB$. Thus, if $D_{AB}$ is known, it may be possible to obtain information about the excitation energy of the metastable fragments. For example, if atom $A'$ happened to be in the ground
state, then $U_A^i$ would be zero and the excitation energy of
the metastable atom $B^m$ could be determined from Eq. (7). In
general, however, fragment excitation energies cannot be
determined from these measurements alone.

1.4 Symmetry Considerations in Molecular Dissociation

Anisotropic distributions of dissociation fragments
can be obtained during the dissociation of molecules orientated
isotropically about an incident electron beam. This experimental
fact immediately suggests that the probability of excitation of
a given molecule is dependent on the relative orientation of
the incident electron beam and some axis of the molecule
(assuming axial recoil). Dunn (Dunn, 1962) has shown that this
result can be qualitatively explained in terms of molecular
state symmetries and symmetry operations. He points out that,
since the interaction potential between an incident electron
and a target molecule is a scalar sum of Coulomb terms, the
symmetry of the total collision system must be conserved.
Using this fact, he was able to consider the excitation of
molecules orientated parallel and perpendicular to the electron
beam. The process of dissociative attachment was of particular
interest during this work, since the absence of an outgoing
electron enabled definite symmetries to be considered. This
work is briefly outlined below.

Consider the incoming electrons to be represented by
the plane wave \( e^{\textbf{ik}_0 \cdot \textbf{r}} \) where \( \textbf{k}_0 \) represents the electron momentum. This will be the case at high energy where the Born approximation is valid.

This incident plane wave is symmetric with respect to all rotations about \( \textbf{k}_0 \) and all reflections in planes containing \( \textbf{k}_0 \). In general, any given molecular state is either symmetric or antisymmetric with respect to one or both of these operations. Thus, if the total symmetry of the system is to remain constant, then knowledge of an initial molecular state symmetry enables something to be said about the final molecular state symmetry. For example, if the initial molecular state was symmetric (or antisymmetric) with respect to rotations about \( \textbf{k}_0 \), then the final molecular state must also be symmetric (or antisymmetric) with respect to rotations about \( \textbf{k}_0 \). Similarly, if the initial molecular state is symmetric (or antisymmetric) with respect to reflections in a plane containing \( \textbf{k}_0 \) then the final molecular state must also be symmetric (or antisymmetric) with respect to such reflections.

Using these symmetry arguments, Dunn was able to construct a table of transition probabilities for the excitation of molecules orientated both parallel and perpendicular to \( \textbf{k}_0 \). These results are shown in Table 1 for homonuclear molecules and in Table 2 for heteronuclear molecules.

It is of interest to note that for molecules orientated parallel to \( \textbf{k}_0 \) the transition probability is zero except for transitions in which \( \Delta \lambda = 0, + + \) and \( - - \). This is true
\[
\begin{array}{cccccccc}
\Sigma^+ & \Sigma^- & \Sigma^+ & \Sigma^- & \Pi^+ & \Pi^- & \Delta^+ & \Delta^- \\
\Sigma^+ & | & | & 0 | 0 & 0 | 0 & 0 | 0 & 0 | 0 & 0 | 0 \\
\Sigma^- & | & | & 0 | 0 & 0 | 0 & 0 | 0 | 0 | 0 | 0 \\
\Sigma^+ & | & | & 0 | 0 & 0 | 0 & 0 | 0 | 0 | 0 | 0 \\
\Sigma^- & | & | & 0 | 0 & 0 | 0 & 0 | 0 | 0 | 0 | 0 \\
\Pi^+ & | & | & x | x & x | 0 & 0 | 0 | 0 | x | 0 \\
\Pi^- & | & | & x | x & x | 0 & 0 | 0 | 0 | x | 0 \\
\Delta^+ & | & | & x | x & 0 | 0 & 0 | 0 | 0 | x | 0 \\
\Delta^- & | & | & x | x & 0 | 0 & 0 | 0 | 0 | x | 0 \\
\end{array}
\]

**TABLE 1.**

Behaviour for alignment of the internuclear axis parallel to the symmetry axis is indicated to the right of the vertical line, perpendicular alignment to the left.

- X - finite transition probability,
- 0 - zero transition probability.

\[
\begin{array}{cccc}
\Sigma^+ & \Sigma^- & \Pi & \Delta \\
\Sigma^+ & x | x & 0 | 0 & x | 0 & x | 0 \\
\Sigma^- & x | x & x | 0 & x | 0 \\
\Pi & x | x & x | 0 | 1 \\
\Delta & x | x \\
\end{array}
\]

**TABLE 2.**

The notation used is as in Table 1.
for both homonuclear and heteronuclear molecules.

In the case of dissociative excitation, the presence of an outgoing scattered electron, with electron momentum $\mathbf{p}_n$, further complicates the above treatment. This problem is partially overcome by assuming that the scattered electron can be represented by a second plane wave. The incident and scattered plane waves can then be combined into a plane wave $e^{i\mathbf{K} \cdot \mathbf{r}}$ where $\mathbf{K} = \mathbf{p}_o - \mathbf{p}_n$ (see Fig. 3). The vector $\mathbf{K}$, which is called the momentum transfer vector, is now the axis of symmetry for the scattering process and the above symmetry arguments may once again be applied. In general, however, the orientation of $\mathbf{K}$ with respect to $\mathbf{k}_o$ will vary depending on the incident electron energy, the energy lost in the excitation process and the angle between $\mathbf{k}_n$ and $\mathbf{k}_o$. This problem does not, however, arise at high electron energies or at energies close to the dissociation threshold, since in both cases the $\mathbf{K}$ direction is well defined. In the former case, for example, $\mathbf{K}$ is perpendicular to $\mathbf{k}_o$. This is due to the predominant forward scattering of high energy electrons. At threshold, however, $\mathbf{k}_n$ is zero and thus $\mathbf{K}$ and $\mathbf{k}_o$ are parallel.

1.5 The Angular Distribution of Dissociation Fragments

A number of workers have made theoretical studies of the angular distributions of dissociation fragments produced by electron impact dissociation of diatomic molecules. The
Fig. 3

The momentum transfer vector and its relation to the momentum of the incident electron and the momentum of the scattered electron.

Fig. 4

CALCULATED ANGULAR DISTRIBUTION OF 430 MEV PROTONS FOR VARIOUS ELECTRON ENERGIES FROM PROTON-MENGUS
first of these studies was made by Kerner (Kerner, 1953) who considered dissociative excitation of molecular hydrogen ions. Zare (Zare, 1967) has examined the same system in greater detail and pointed out a number of errors in the original work of Kerner. A number of more general treatments of molecular dissociation have also been presented. In particular, the treatments of Van Brunt (Van Brunt, 1970) and Newell (Newell, 1970) are of interest. Since these treatments closely follow the work of Zare and Kerner a brief outline of Zare's work is presented below.

Consider the excitation of a molecule from the ground state $u_0$ to some repulsive state $u_n$. After the excitation, the molecule will dissociate and the fragments will come apart with some relative kinetic energy. If the 'axial recoil' approximation is assumed, then the fragments will move off in the direction of molecular vibration. During the excitation the colliding electron undergoes a momentum change which is given by

$$\hbar \mathbf{K} = \hbar \mathbf{k}_0 - \hbar \mathbf{k}_n$$  \hspace{1cm} (8)

where $\hbar \mathbf{k}_0$ is the initial electron momentum and $\hbar \mathbf{k}_n$ is the final electron momentum. The direction of the incident electron is specified by $\mathbf{k}_0$ and the direction of the scattered electron is specified by $\mathbf{k}_n$. The differential cross-section for this scattering process can be completely specified in terms of the momentum transfer vector $\mathbf{K}$ and the target
molecule's orientation with respect to \( \mathbf{k} \). Thus the differential cross-section for scattering an electron from the \( k_o \) direction into the \( k_n \) direction, during the excitation of a molecule orientated at polar angles \( \theta \) and \( \phi \) with respect to \( \mathbf{k} \), is given by

\[
\sigma_k(\theta, \phi) = \frac{k_n}{k_o} | f_k(\theta, \phi) |^2
\]  

(9)

where \( f_k(\theta, \phi) \) is the associated scattering amplitude. The above scattering amplitude can, in general, be evaluated using the Born approximation.

Upon dissociation of the excited molecule the dissociation fragments move off in the \( \theta, \phi \) direction (assuming axial recoil). Thus the above differential cross-section for electron scattering is also a partial differential, cross-section for molecular dissociation. In accordance with Eq. (9) this partial differential cross-section for dissociation can be written

\[
I_k(\theta, \phi) = \frac{k_n}{k_o} | f_k(\theta, \phi) |^2
\]  

(10)

In order to obtain the total differential cross-section for dissociation into some laboratory direction \( \mathbf{k}, \mathbf{q} \), it is necessary to express the above partial differential cross-section in terms of this direction. Zare (Zare and Herschbach, 1963) (Zare, 1967) has performed the necessary transformation and shown that for dipole allowed transitions Eq. (10) can be expressed in the following way:
\[ I_K(\chi, \phi) \sim \cos^2(\chi)\cos^2(\chi') + \frac{1}{2}\sin^2(\chi)\sin^2(\chi') \] (11)

for \( \Delta \lambda = 0 \) (i.e. \( \Sigma \rightarrow \Sigma, \pi \rightarrow \pi \), etc.) and 

\[ I_K(\chi, \phi) \sim \sin^2(\chi)\cos^2(\chi') + \frac{1}{2}(1 + \cos^2\chi)\sin^2(\chi') \] (12)

for \( \Delta \lambda = \pm 1 \) (i.e. \( \Sigma \rightarrow \pi, \pi \rightarrow \Delta \), etc.).

\( \chi \) and \( \phi \) now correspond to the direction of the dissociation fragments with respect to \( k_o \) and \( k' \) corresponds to the included angle between \( k_o \) and \( K \). These relations apply for a fixed magnitude but arbitrary direction of \( K \).

In order to obtain the total differential cross section for dissociation, it is necessary to integrate \( I_K(\chi, \phi) \) over all directions and magnitudes of \( K \). This is necessary because different orientations of \( K \) with respect to \( k_o \) also result in dissociation fragments travelling in the \( k, \phi \) direction. However, at electron energies close to the dissociation threshold, the integration is greatly simplified by the fact that \( k_o \) and \( K \) are then parallel and the magnitude of \( K \) remains approximately constant. It thus follows from Eqs. (11) and (12) that:

\[ I(\chi, \phi) \sim \cos^2(\chi) \] (13)

for a \( \Delta \lambda = 0 \) transition and

\[ I(\chi, \phi) \sim \sin^2(\chi) \] (14)

for a \( \Delta \lambda = \pm 1 \) transition

where \( I(\chi, \phi) \) is the total differential cross-section for
dissociation near threshold.

At higher electron energies, however, the total differential cross-section has a more complicated form since $\xi'$ has a range of values and $K$ has a range of magnitudes. Zare (Zare, 1967) has done the necessary integration and has evaluated the total differential cross-section for 4.38 eV protons produced during the dissociation of $H_2^+$. His results for incident electron energies ranging from 15 eV to 3000 eV are shown in Fig. 4. At 15 eV the electron energy is fairly close to threshold and the expected $\cos^2(\xi)$ distribution is obtained. However, as the incident electron energy is increased the angular distribution of protons becomes more and more isotropic until finally the minimum at $\xi = 90^\circ$ becomes a broad maximum. At first sight this behaviour seems unusual since at high electron energies $K$ and $k_o$ are perpendicular and one would expect a $\sin^2(\xi)$ distribution. Zare points out that this seemingly paradoxical behaviour is due to the dependence of $T_K(\xi, \phi)$ on $K$. This dependence strongly weights the small values of $K$ in the integration. These small values of $K$ correspond to $\xi' \sim 0^\circ$ and thus the total differential cross-section is strongly weighted by $\cos^2(\xi)$ terms. Zare's theoretical results for molecular dissociation seem to agree quite well with published experimental data.

In all the above arguments the axial recoil approximation was assumed to be valid. This will be the case where the final dissociative state of the molecule is strongly repulsive.
However, in many cases the dissociation fragments part with such low kinetic energies that molecular rotation must also be considered. The effect of this rotation is to produce a blurring of the distribution expected under axial recoil conditions.

It is of interest to note that Zare and Herschbach (Zare, 1963) have obtained results similar to those of Eqs. (13) and (14) for the photodissociation of diatomic molecules. They found that the differential cross-section for photodissociation was given by

\[ I(\chi, \phi) \propto |\mathbf{e} \cdot \langle \mathbf{M} \rangle|^2 \]  

(15)

where \( \chi \) and \( \phi \) are measured with respect to \( \mathbf{e} \) the electric vector of the incident beam of polarized photons and \( \langle \mathbf{M} \rangle \) is the dipole matrix element for the transition involved. This equation leads to Eq. (13) when the dipole moment lies along the internuclear axis and leads to Eq. (14) when the dipole moment lies perpendicular to the internuclear axis. These two cases correspond to transitions in which \( \Delta \Lambda = 0 \) and \( \Delta \Lambda = \pm 1 \) respectively.

1.6 Fragment Kinetic Energy Shifts due to Momentum Transfer

During an electron collision some of the momentum of the impinging electron is transferred to the target molecule. The molecule then acquires an additional velocity in the
direction of the electron beam. This additional velocity is a maximum at threshold since all the electron's momentum is then acquired by the molecule. Van Brunt (Van Brunt, 1970) has considered the energetics of this process for dissociation at threshold and has shown that the difference in observed kinetic energy of fragment B"\(\text{H}\), when observed at angles \(\kappa\) and \(\pi - \kappa\), with respect to the electron beam, is given by

\[
\Delta W_B(\kappa) = \frac{4}{M_A/M_B} \left[ \frac{m_e E W_B^0}{M_B} \right] \cos \kappa. \tag{16}
\]

In this equation \(M_A/M_B\) is the fragment mass ratio, \(m_e\) is the electron mass, \(E\) is the electron energy at threshold, and \(W_B^0\) the observed kinetic energy of B"\(\text{H}\) at \(\kappa = \pi/2\).

This shift is very small for all but the lightest of fragments and was not observed during the present work.
CHAPTER 2

A REVIEW OF SOME EXPERIMENTAL APPROACHES
TOWARDS METASTABLE EXCITATION AND DETECTION
2.1 Introduction

In this chapter some of the experimental techniques currently being used to study metastable atoms and molecules are considered. In general, these experiments can be classified in terms of the mode of excitation and the method of detection. In the four subsections of section 2.3 a number of typical experiments are classified according to this scheme.

2.2 Direct and Indirect Detection of Metastable Atoms and Molecules

Metastable atoms and molecules, with sufficient internal energy, can cause Auger electron emission from special surfaces and can thus be directly detected. Alternative processes, such as electric field and surface ionization, also enable the direct detection of these atoms and molecules. However, such direct detection does not itself enable identification of the individual states involved. This problem is partially overcome in electron impact experiments since it is then possible to directly measure the excitation energy of molecular metastable states and the dissociation limits of fragment parent states. However, as noted in Chapter 1, such studies do not necessarily provide direct information on the excitation energy of metastable fragments. In order to unambiguously and directly identify these fragments, a different detection technique must be used.

Metastable atoms and molecules can be indirectly detected by observing the photons produced during their radiative
decay. This mode of detection, unlike the above, does enable the direct identification of metastable fragment states. For example, the metastable state \( \text{O}^1\text{S} \) can be both detected and identified by its 5577Å fluorescence. This detection technique has been used in the study of metastable fragments produced by both electron and photon excitation. Its success does, however, depend on the lifetime of the metastable fragments and their kinetic energy. A very short lifetime, for example, may mean that almost all the decay occurs before the fragments can be viewed by the detector and too long a lifetime may mean that little or no decay occurs at all. In practice, this means that a given apparatus can only detect those metastable fragments with lifetimes which lie within a certain range.

2.3 A Review of Some Experiments which Utilize Different Techniques of Metastable Excitation and Detection

2.3.1 Direct Detection Following Excitation by Electron Impact

A typical time-of-flight apparatus, which displays the features of this type of experiment, has been described by Freund and is shown in Fig. 5 (Freund, 1973). Three detectors were available which allowed detailed study of high-Rydberg fragments, metastable atoms and molecules and photons. The high-Rydberg detector utilized both the electric field and surface ionization of high-Rydberg fragments. Other metastable atoms and molecules, with sufficient internal energy, were detected by an Auger detector. A pulsed electron beam was used to excite
Fig. 5
An apparatus which features direct detection following excitation by electron impact.

Fig. 6
An apparatus featuring indirect detection following excitation by electron impact.
the molecules of a gas beam and charged particles were removed by electrostatic deflector plates. The use of a well defined molecular beam enabled the spread in fragment energies, due to random thermal motion, to be reduced.

Another time-of-flight apparatus, which utilizes surface ionization for the direct detection of metastable atoms and molecules has been described by Johnson (Johnson, 1973). Excitation was again by electron impact and during the course of the investigation, both a diffuse gas target and a molecular beam were used. Lifetime and electric field quenching measurements enabled identification of the metastable fragment states. The lifetime measurements were made by directly observing the change in fragment signal intensity, due to in-flight radiative decay, at two positions along the flight path. The quenching was performed by passing the fragments through a variable electric field.

Borst and Zipf describe an apparatus for measuring the lifetimes of thermal energy metastable molecules after excitation by electron impact. (Borst, 1971). In this experiment the metastable molecules were directly detected by an Auger detector and the lifetimes were deduced from the shape of the time-of-flight spectrum.

2.3.2 Indirect Detection Following Excitation by Electron Impact

An apparatus which enables observation of radiative decay from both metastable and non-metastable states, has been
described by Freund. (Freund, 1969). This apparatus which utilized excitation by electron impact, is shown in Fig. 6. A molecular beam was excited by electron impact and the photons produced were transmitted, by a monochromator, to a photomultiplier. An aluminized mirror could be placed in front of the spectrometer in order to observe the radiation originating from the electron bombarder region (i.e. the radiation from non-metastable states). Metastable atoms and molecules, which drifted into the detector chamber before radiating, could be detected by removing this mirror. Careful shielding of the monochromator during these measurements, prevented detection of the photons from non-metastable states. The emission spectra from metastable and non-metastable states were studied by exciting the gas molecules with a continuous electron beam. Time-of-flight measurements were made using a pulsed electron beam.

2.3.3 Direct Detection Following Excitation by Photon Absorption

Gilpin and Welge describe a time-of-flight experiment, in which a continuum light source was used to excite a gas target. (Gilpin, 1971). In this experiment only a short wavelength cut-off was attempted and hence the very large spread in photon energy made identification of fragment parent states difficult. The use of a variable short wavelength cut-off did, however, enable the identification of some metastable fragment states. The variable short wavelength cut-off was obtained by the use of LiF, CaF₂, BaF₂ and sapphire windows. An afterglow tail, which
accompanied the main light flash, was also reported. The metastable fragments produced during the experiment were directly detected by Auger electron emission at a caesium surface.

A Photofragment Spectrometer has been described by Wilson and is shown in Fig. 7 (Wilson, 1970). Three different light sources were used with this apparatus and the fragments were detected by a mass spectrometer after ionization. This detection technique enables the direct detection of both metastable and non-metastable dissociation fragments. However, as yet, only non-metastable fragments have been studied using the apparatus.

A Theta Pinch light source was used to produce a continuum across the visible and U.V. regions and thus enabled study in the region of greatest photochemical interest: the middle U.V. Unfortunately, the low intensity of this light source, after polarization and wavelength selection, remained a serious problem. This problem was overcome by the use of a pulsed solid state laser system (Fig. 8) and frequency doubling enabled a number of different photon energies to be obtained. Rotation of the plane of polarization made angular studies of a given dissociation process possible. The light fluxes obtained using this system were more than an order of magnitude higher than those obtained using the continuum source, but in general, the low photon energy limited the systems application. A tunable dye laser was also available, but once again the most interesting spectroscopy lay outside its photon energy range.
Cutaway drawing of photofragment spectrometer. The beam of molecules to be photodissociated enters from the left and is crossed perpendicularly by pulses of polarized light, usually from a laser. The photodissociation fragments which recoil upward are detected by a mass spectrometer as a function of mass, of photon energy, of photon flux, of time after the laser pulse, and of angle of recoil θ measured from the electric vector of the light. (The θ shown in the drawing would be a negative angle of recoil.) The interaction region and the mass spectrometer are in separately pumped chambers connected by a small liquid nitrogen (LN₂) cooled tube, which collimates the fragments. The numbered components are 1—port for laser beam, 2—lens to match diameter of laser beam to that of molecular beam, 3—outer wall of bakable ultrahigh vacuum chamber, 4—LN₂ cooled fragment collimating tube, 5—mass spectrometer electron bombardment ionizer, 6—mass spectrometer electron multiplier, 7—quadrupole section of mass spectrometer, 8—LN₂ cooled partition between interaction and detection chamber, 9—interaction region, 10—LN₂ cooled molecular beam collimator and oven shield, 11—LN₂ cooled inner wall of interaction chamber, 12—molecular beam oven with capillary slits, and 13—molecular beam port.

Side view of photofragment spectrometer. The laser and molecular beams intersect in an interaction chamber, and photodissociation fragments which recoil upward are detected by a quadrupole mass spectrometer in a separately pumped detection chamber. The Q-switched ruby or neodymium-glass laser assembly is shown with the following components: A—lens to adjust size of laser beam to match diameter of molecular beam, B—polarization rotator (half-wave plate or double Fresnel rhombs) adjustable under computer program control, C—second harmonic generator (ADP or KDP crystal), D—front reflector, E—laser rod and pumping flash lamp, F—polarizer (calcite Glan prism), G—adjustable aperture, H—Q switch (Pockels cell), I—rear reflector, and J—light monitor (photodiode). The laser assembly rests on a bench whose position is adjustable with respect to the rest of the spectrometer. Other components of the spectrometer are: 1—500 liter/sec ion pumps, 2—gate valves, 3—port for light beam, 4—liquid nitrogen (LN₂) cooled stainless steel cryogenic liners, 5—resistance heated titanium sublimation pump, 6—electron bombardment heated titanium sublimation pump, 7—ion pump (typical of three), 8—molecular beam oven (passing into the plane of the paper), 9—LN₂ cooled fragment collimating tube between interaction and detection chambers, 10—LN₂ cooled baffle separating interaction and detection chambers, 11—electron bombardment ionizer of mass spectrometer, 12—quadrupole section of mass spectrometer, and 13—Cu-64 72-stage electron multiplier.
2.3.4 Indirect Detection Following Molecular Excitation by Photon Absorption

An experiment of this type has been reported by Lawrence and McEwan (Lawrence, 1973). The apparatus, which was used to measure the quantum efficiency for the production of O(1S) by photodissociation of O₂, is shown in Fig. 9. Light from a pulsed discharge lamp was passed through a grating monochromator and then into the photolysis cell. A photomultiplier, mounted behind a sodium salicylate screen, monitored the incident beam intensity and also recorded the O₂ absorption at different wavelengths. The wavelengths used corresponded to the discrete lines emitted by the hydrogen or argon filled flash lamp. The 5577 Å fluorescence, from the O(1S) metastable state, was detected by a photomultiplier mounted behind a yellow glass filter. The fluorescence could be measured since it occurred after the initial photon pulse had died away. The relative quantum yield, at a particular wavelength, was calculated by dividing the number of O(1S) atoms detected by the number of photons absorbed. A similar experiment has been described by Ridley (Ridley, 1973).
Fig. 9

An apparatus featuring indirect detection following excitation by photon absorption.
CHAPTER 3

EXPERIMENTAL CONSIDERATIONS
3.1 Introduction

This chapter deals in detail with a description of the present experimental arrangement and its associated data accumulation systems. Apparatus performance and special experimental techniques are also discussed. For clarity a brief review of the whole experiment is presented before these detailed considerations.

3.2 A Review of the Experiment

The time-of-flight experiment involved exciting the molecules of a diffuse-gas target, with a pulse of approximately monoenergetic electrons (see Section 3.5), and then recording the resulting fragment signal as a function of its arrival time at the detector. This technique enabled photons, fast atomic and molecular metastable fragments and thermal energy metastable molecules to be separately resolved in the time-of-flight spectrum. Only fragments with sufficient internal energy to cause Auger electron emission from special surfaces were detectable. Radiative decay from atoms and molecules in non-metastable states rendered them undetectable and the use of electric and magnetic fields to deflect charged particles, from their path to the detector, prevented ion and electron detection. During the flight to the detector, radiative decay from some metastable states also occurred and thus prevented the direct detection of some fragments. Thus, only photons and neutral metastable atoms and molecules, arriving at the detector, were detected. A typical time-of-flight
spectrum is shown in Fig. 10.

The flight path from the electron beam to the detectors covered a distance of $41.3 \pm 0.5$ cm and careful measurements of fragment flight times, over this distance, enabled calculation of the corresponding fragment kinetic energies. A coordinate transformation was then performed and where possible, the fragment signal intensity was plotted against the total kinetic energy released during the dissociation.

Excitation functions, which are recordings of signal intensity against electron energy at fixed time-of-flight, enabled the electron energy at fragment appearance (threshold potential) to be determined. This information enabled calculation of the dissociation limit of the fragment parent states (see Eq. (6) of Chapter 1).

State symmetry was investigated by plotting signal intensity at fixed time-of-flight, as a function of the angle between the electron beam and the flight path.

Secondary processes such as the collision of an electron with more than one gas molecule and the collision of metastable fragments with parent gas molecules, were avoided by careful choice of both gas pressure and electron current. Plots of signal intensity against gas pressure and electron current were used in order to select the best operating conditions. These plots become non-linear if a significant number of secondary collisions take place.
3.3 **Description of the Apparatus**

3.3.1 **The Vacuum System**

The vacuum system (Fig. 11) consisted of a two chamber, rectangular stainless-steel box which housed the electron gun in one chamber and the detector system in the other. The two chambers were pumped independently by two 6" mercury diffusion pumps and standard backing line equipment. Liquid air cooled traps were used in conjunction with these pumps.

The larger of the two chambers housed the detector system and because of possible surface contamination problems was designed for ultra-high vacuum. This involved the use of indium seals for flanges and special rotary feedthroughs for the butterfly valves. The chamber could be baked using an internally mounted quartz-halogen heating lamp. The detector system was mounted on a centrally located, liquid nitrogen cooled, copper finger. A pair of parallel electrostatic deflector plates were mounted in this chamber to deflect any charged particles from their path to the detector.

The smaller chamber, which was used to house the electron gun, was connected to the detector chamber by a narrow bore tube. This tube, lying along the central horizontal axis of the apparatus, allowed the passage of metastable fragments while enabling a pressure differential to be maintained between the two chambers. A gold mesh, attached to a screw-in aperture, could be biased to prevent positive ions entering this tube and reaching the detectors. The tube could be blocked off by closing a 2"
Fig. 11. The Vacuum System (1/4 Scale)
butterfly valve located in the separating wall. Gas could be leaked at a constant rate (variable) into the small chamber through a bakeable leak valve. The addition of a 6" baffle valve, between the diffusion pump and the cold trap, allowed this leaked gas to be cryogenically pumped while isolating it from the diffusion pump. Viton seals were used in this chamber and baking was again by means of an internally mounted quartz-halogen lamp.

The pressure in both chambers was measured by Ion gauges and in addition a Pirani gauge was available for pressure measurement in the small chamber. The ultimate background pressure achieved in the detector chamber was $5 \times 10^{-9}$ torr after baking and cryogenic pumping by the cold finger. Although ultra-high vacuum was not achieved in this chamber, due to outgasing problems, the background pressure was sufficiently low to perform the experiment. The ultimate background pressure obtained in the small chamber was $6 \times 10^{-7}$ torr after baking. Both these background pressures were readily obtained after pumping for 24 hours.

3.3.2 The Electron Gun

The stainless-steel, magnetically focused, electron gun (Fig. 12) was mounted between the poles of a large (800 gauss) permanent magnet, in such a way that the magnetic field lines ran parallel to the electron beam direction. Three electrostatic focusing electrodes assisted this focusing. Electrons were accelerated from a negatively biased cathode to a grounded
electrode and then entered the grounded interaction region. The electrons were collected in two concentric, cylindrical, Faraday cups which allowed beam dispersion to be monitored. To reduce any electron reflection, the outer cylinder was blackened with soot and the shielded inner cylinder biased a few volts positive. The normally inhibited electron beam was pulsed on by driving the first electrode from negative to positive, with respect to the cathode, and turned off by returning its potential to the original negative value. A tungsten grid, over the hole in this electrode, helped to sharpen the electron pulse profile. Directly or indirectly heated cathodes could be mounted in the gun as required. Electrode location and spacing was by ruby balls and the gun was held together by three retaining rods. The shaped electrodes prevented insulator contamination while maintaining good pumping around the cathode. The electron beam was positioned in the same horizontal plane as the central axis of the apparatus and could be rotated, in this plane, about the centre point of the interaction region. This was achieved by rotating the permanent magnet using a rotary feedthrough. Using this set up the angle between the electron beam and the central axis of the apparatus could be varied continuously from $\theta = 45^\circ$ to $\theta = 135^\circ$. Electron gun performance is discussed in Section 3.5 of this chapter.

3.3.3 The Detector System

The double detector system (Fig. 13) consisted of two surfaces from which Auger electrons could be ejected by metastable
fragments and photons. The ejected electrons were separately accelerated and then detected by two channeltron electron multipliers. It was hoped that the low work function surface (Ag – O – Cs), which was obtained by breaking open a photodiode tube in vacuum, would enable the detection of metastable fragments with low internal energy (<5eV). The higher energy fragments, which could eject electrons from both surfaces, were detected by the less sensitive Cu/Be surface. This enabled signal subtraction to yield the low energy fragment contribution. The detector mount, which was constructed from copper, was attached to a cold finger to reduce thermal emission of electrons from the low work function surface. It was positioned so that approximately the same fraction of metastable fragments, traversing the known distance between the gun interaction region and the detector, arrived at each sensitive surface. The two channeltrons were partially shielded from stray magnetic fields by mounting them inside conetic boxes and the ejected electrons were accelerated and directed into these boxes by a tungsten grid mounted on each box. The channeltrons were mounted with their earthed cones immediately behind these grids. A copper plate between the two detectors prevented electrons from either surface being detected by the wrong channeltron. The shielded, high voltage channeltron cables were fed by a smoothed 3 Kilovolt D.C. power supply and the data pulses, from each detector, separately passed to two high input/low output impedance preamplifiers. Despite this, simultaneous data taking using both detectors,
although possible, was not attempted due to data storage limitations. The high voltage was disconnected from the channeltron not in use. The preamplified data pulses were amplified and discriminated before being counted.

The scratch-weakened glass envelope was removed from the photodiode under vacuum by heating a tungsten wire which surrounded it. The envelope then fell with the aid of weights from the inverted photodiode, into a stainless-steel cradle in the bottom of the chamber.

Detector performance is discussed in Section 3.5 of this chapter.

3.4 The Apparatus Electronics and Data Accumulation Systems

3.4.1 The Electron Gun Pulsing Mode

The normally inhibited electron beam was pulsed on by driving the first electrode of the electron gun from negative to positive with respect to the cathode. A variable width pulse of suitable voltage for this purpose, was delivered by a triggered pulser approximately every two milliseconds. This low repetition rate allowed sufficient time between electron pulses for low energy metastable molecules to reach the detector. The pulser was triggered either by a 2\(\mu s\) computer generated pulse or by the initial rise of a signal generator square wave. The accelerating potential and the other electrode voltages were supplied by two smoothed D.C. power supplies. The electron gun circuit is shown in Fig. 14.
During the pulsed operation of the electron gun the necessary current normalization proved difficult so a charge normalization technique was developed. This involved slowly charging a 150\mu F tantalum capacitor with charge from the gun collectors, until its voltage reached a small preset level. When this level was reached the capacitor was quickly discharged. This slow charging and quick discharging cycle was repeated throughout data taking and the number of complete chargings counted by a scaler. To accomplish this the voltage across the capacitor, which was measured and amplified by an electrometer, was used to switch on a Comparator circuit when it reached the preset level. This circuit then shorted out the capacitor and delivered a suitable pulse to the scaler for counting. The capacitor voltage was only allowed to reach a few millivolts in order to prevent it affecting the electron energy. The advantage of recording the total charge passed by the gun during data taking was that electron current instabilities could then be completely ignored. The main cause of these instabilities was cathode contamination which caused the electron current to disappear for several minutes at a time. Small changes in electron current also occurred with change in electron energy, but once again, normalizing with respect to charge removed the necessity for the current to remain stable.

3.4.2 Manual Time-of-Flight Data Accumulation

A variable width pulse from a delay unit was used to
gate a scaler during manual data taking. This window enabled metastable fragments with a known range of flight times, from the interaction region to the detectors, to be counted. Counting was inhibited during the absence of this pulse. Each time the electron gun pulsed the synchronised delay unit went through a preset delay time before delivering the gate pulse to the scaler. The Time-of-Flight Spectrum was obtained by plotting signal intensity against delay time at constant gas pressure. Signal normalization was achieved, at each delay setting, by allowing data to accumulate for a known number of chargings of the collector capacitor. The signal accumulation time was always very long compared with the time between electron pulses. Signal intensity at fixed time-of-flight was also measured as a function of both gas pressure and electron beam angle.

The limited resolution and poor statistics which resulted from manual data accumulation led to more automatic systems and longer accumulation times.

3.4.3 **Time-of-Flight Data Accumulation by Pulse Height Analyser**

The use of a Time-to-Amplitude Converter (T.A.C.) and a Pulse Height Analyser enabled increased time-of-flight resolution and automatic data taking. The T.A.C. was started a short time after each electron pulse to prevent preferential detection of the abundant photons. A 500 nanosecond discriminator pulse from the synchronised delay unit was used for this purpose. The first pulse from the detector discriminator was used to stop the T.A.C.
and its output pulse voltage, which was proportional to the time
between the start and stop signals, was pulse height analysed.
This enabled signal intensity against time of flight to be
recorded and displayed directly. As the probability of producing
more than one detectable atomic fragment per electron pulse was
very low, there was no preferential recording of the fast fragments.
Pile up corrections were found to be unnecessary. Data accumula-
tion times varied from several hours to several days. Different
time-of-flight spectra could be charge normalized to each other
by accumulating data for the same number of chargings of the
collector capacitor. A gate unit which cut off the start pulse
to the T.A.C., after a preset number of these chargings, auto-
matically terminated data taking at the right time. The logic
signal for this purpose was supplied by the scaler. This system
of data accumulation is shown schematically in Fig. 15.

The main disadvantage of this system of data accumulation
was that data count rates had to be kept lower than one count per
electron pulse to prevent fast fragment pile up. A further
disadvantage was that only 80μs portions of the complete time-of-
flight spectrum could be studied at one time.

The data was punched onto paper tape and could be read
into a PDP-8/E computer for display and analysis.

3.4.4 Time-of-Flight Data Accumulation by Computer
To enable the whole time-of-flight spectrum to be recorded
at one time and to allow data count rates to exceed the gun pulsing
Fig. 15. Three Modes of Automatic Data Accumulation
rate, the experiment was placed on line to a PDP-8/E computer by a special hardware interface. This computer controlled interface delivered a triggering pulse to the electron gun pulser and then after a preset delay time accumulated data counts in one of two identical buffers. After a preset channel width time, the incoming data pulses were channeled into the other buffer and the total count in the first buffer deposited into the memory. On completion of the next time interval, the incoming data pulses were channeled to the now empty first buffer and the total count in the second buffer deposited in memory at a new address. This process enabled metastable fragments with a fixed range of flight times to be recorded at a particular memory address. Using this two buffer system, there was no loss of data during the time taken to deposit the buffer count into the 256 time channels. Upon completion of the 256 channel scan the data accumulation was terminated and after a further delay the electron gun was pulsed again. The gun repetition rate allowed sufficient time between electron pulses for the slow metastable molecules to reach the detector. The complete cycle was repeated with a frequency of about 500 Hz and data accumulation times varied from several hours to several days. Different time-of-flight spectra could be charge normalized to each other by accumulating data for the same number of chargings of the collector capacitor. The gate unit was used to cut off the incoming signal when a preset number of chargings was reached. This system of data accumulation is shown schematically in Fig. 15.
The displayed time-of-flight spectrum could be averaged and expanded as required. Background subtraction and count integration were also available options. The time-of-flight spectrum could be reproduced on paper using a point plot routine and the data could be punched onto paper tape for storage.

As the computer was not located in the same room as the experiment, it was necessary to amplify and discriminate the incoming data pulses at the interface location as well as at the experiment.

The maximum time resolution possible using this data taking system was limited by the speed at which the PDP-8/E could carry out instructions. In practice, this limit was 2.5μs (two instructions). This time limit was utilized to best advantage by the addition of hardware which permitted direct access to the computer memory.

3.4.5 Excitation Function Data Accumulation

Excitation functions were recorded on a multichannel scaler by automatically recording signal intensity, at fixed time-of-flight, as a function of electron energy. An output voltage proportional to the channel address was used to ramp a power supply which in turn ramped the electron energy through the required range. The data counts resulting from a particular electron energy were all recorded in the same channel. A variable width gate pulse from the synchronised delay unit enabled
fragments with a known range of flight times to be recorded. To charge normalize the data, the channel address was advanced by a pulse from the Comparator after each complete charging of the collector capacitor. The charging time was always long compared with the time between electron pulses. This technique removed the problem of the change in electron current which resulted at certain electron energies. After scanning through all the channels, the accumulated data could be either displayed or another scan automatically initiated. This system of data taking is shown schematically in Fig. 15. The data was then punched onto paper, tape for storage.

3.5 Apparatus Performance and Special Experimental Techniques

3.5.1 The Electron Gun Performance

In order to ensure good electron collection, the inner Faraday cup of the electron gun was biased positive with respect to ground. In order to obtain the best voltage for this purpose the charge collected per unit time was plotted as a function of this bias voltage. The resulting curve, obtained at an electron energy of 10 eV, is shown in Fig. 16. The curve is seen to rise with increasing voltage until a current plateau is reached. From this plateau a bias voltage of + 10 V was chosen. Since this voltage is fairly small, it has little effect on the well shielded interaction region. In any case, such effects are automatically taken into account by energy calibration procedures. The electron gun was operated in its normal pulsed mode during this investigation.
Plots similar to the one shown in Fig. 16 were also obtained at a number of different electron energies. It was generally found that electron collection improved with increasing electron energy. For example, at an electron energy of 100 eV the collector current was found to be independent of any applied bias voltage.

Electron beam dispersion was monitored by recording the electron current collected by the outer Faraday cup. The gun was operated in a D.C. mode during this investigation in order to obtain a detectable current at this collector. The resulting current is plotted as a function of electron energy in Fig. 17. The current is seen to remain zero until an electron energy of about 75 eV is reached. Above this electron energy the electron current is seen to rise almost linearly. However, it should be noted that even at high electron energy this current is only about one thousandth of the current collected by the inner Faraday cup. This shows that the electron beam remains well focused over the range of electron energies used during the experiment. The inner Faraday cup was biased at +10 V during this work.

The electron pulse shape was monitored by observing the pulse of prompt photons produced during the electron impact excitation of Helium atoms. This was done by starting the Time-to-Amplitude Converter in coincidence with the start of the electron pulse. The resulting photon pulse shapes, obtained at two different electron pulse width settings, are shown in Fig. 18. It can be seen from this figure that the 10 μs electron pulse is
Fig. 18

The electron pulse profile at two different width settings.
of the expected width and that both pulses exhibit a sharp cut-off. During this work it was necessary to reduce the photon signal in order to prevent signal pile-up at the beginning of the electron pulse. Careful choice of both gas pressure and electron current enabled the photon signal to be reduced to the required level.

The electron energy scale was calibrated by recording an excitation function for the production of Helium atoms in the $2^3S_1$ metastable state. This process is particularly suitable for calibration purposes since its excitation cross-section can be approximated to a step function. This step function rises steeply at an excitation threshold of 19.81 eV (Pichanick, 1968). This excitation threshold can be used to calibrate the incident electron energy scale. Furthermore, comparison of the experimentally obtained excitation function, with its expected step function behaviour, enables an estimate to be made of the spread in incident electron energy.

A typical He$^+$ excitation function is shown in Fig. 19. The centre point of the linear portion of this excitation function should correspond to an electron energy of 19.81 eV. However, the actual position of this centre point, as read from the figure, corresponds to an electron energy of 19.9 eV. This small discrepancy is probably caused by contact potentials in the electron gun circuit. In addition, analysis of the initial rise of this excitation function suggests that the electron beam has an energy spread of about 1 eV (F.W.H.M.). This estimate
was made by assuming that the electron energy distribution function is rectangular in shape. However, the initial curvature of the excitation function suggests that the actual distribution function has a more complex form.

Where necessary, the excitation functions presented in this thesis are corrected for contact potential effects.

3.5.2 Preparation of the Low Work-Function Detector and General Detector Performance

In order to prevent contamination of the low work-function detector, it was necessary to take a number of precautions before removing its protective glass envelope. A typical preparation procedure is briefly outlined below.

1. The detector chamber was pumped and baked for several days prior to exposure of the low work-function surface.

2. The detector system was then cooled to liquid nitrogen temperatures in order to reduce the chamber pressure to an absolute minimum.

3. An inert gas (usually Argon) was leaked into the apparatus to a pressure equal to that of the gas filled photodiode tube. (This inert gas acted as a buffer to any contaminant gas molecules produced during rapid heating of the glass envelope and tungsten wire.)

4. The tungsten wire was rapidly heated until the glass envelope fell from the inverted photodiode.

5. The apparatus was quickly pumped down to its original base pressure.
Unfortunately, at the present time, little quantitative information is available about the working lifetime of this detector. However, for a period of several weeks, the detector did remain sensitive to photons entering the chamber through a glass window (i.e. \( \lambda > 3800 \text{Å} \)). This result suggests that the working lifetime of such a detector is quite long. Furthermore, it was discovered that a brief exposure to atmospheric pressure had little effect on this behaviour. Repeated exposure did, however, result in a loss of sensitivity. Despite this, it is likely that a completely contaminated photodiode surface remains more sensitive to low energy metastable fragments than a similar Cu/Be surface.

Despite some initial problems with thermal emission, the low work-function detector was found to perform extremely well. The Cu/Be detector, which was used to detect metastable fragments with fairly high excitation energies, was also found to perform extremely well. Unfortunately, it was discovered that both detectors were affected by rotation of the electron gun's focusing magnet. This rotation was found to produce abrupt changes in signal intensity during the study of isotropic distributions of metastable Helium atoms. Changes in magnetic field orientation, at the detector position, were found to be responsible for these abrupt changes. At the present time, this problem has not been overcome and thus angular distributions of dissociation fragments are not presented in this thesis. The data presented in the following chapters was obtained by setting \( \theta = 90^\circ \).
3.6 Degradation of the Time-of-Flight and Kinetic Energy Resolutions

Freund (Freund, 1973) has made a quantitative study of the factors which are responsible for degradation of the time-of-flight resolution. As may be expected, the most significant cause of this degradation is the use of a finite width electron pulse and a finite width time-of-flight window. For good time-of-flight resolution it is necessary to reduce the width of both of these pulses. Unfortunately, such a width reduction necessarily involves a significant loss in signal intensity. This loss in signal intensity is a serious problem when recording excitation functions near threshold. It is often necessary to sacrifice some time-of-flight resolution in order to improve this signal intensity. The excitation functions reported in this thesis were obtained by using a 10 μs electron pulse and a 10 μs time-of-flight window. Using this setup it was necessary to accumulate data for several days and thus it was not practical to significantly reduce these pulse widths.

The time-of-flight slit function produced by a combination of a 10 μs electron pulse and a 10 μs time-of-flight window is triangular in shape and has a base width of 20 μs (see Appendix 1). However, it is fairly easy to show that the standard deviation of such a triangular distribution function is only 4 μs (i.e. 0.2 times the base width). Unfortunately, the corresponding uncertainty in the calculated fragment kinetic energy is somewhat more significant since the calculation involves a $\frac{1}{t^2}$ term. This uncertainty can be obtained by
simple differentiation and is given by

\[ \frac{\Delta W_B}{W_B} = \frac{2\Delta t}{t} \quad (17) \]

where \( \Delta W_B \) is the uncertainty in the kinetic energy of fragment B and \( \Delta t \) is the corresponding uncertainty in its time-of-flight. For a typical time-of-flight of 65 \( \mu s \) the above consideration results in a 12\% uncertainty in \( W_B \).

A somewhat better time-of-flight resolution was obtained during time-of-flight data accumulation since a narrower electron pulse and a narrower time-of-flight window could be used at the higher electron energies involved. The pulses were typically 3 \( \mu s \) wide and thus an uncertainty of \( \pm 1.2 \mu s \) was introduced into the time-of-flight measurements. This introduces a 5\% uncertainty into the calculated value of \( W_B \) for a fragment flight time of 50 \( \mu s \).

Time-of-flight and kinetic energy resolutions are also degraded by the thermal motion of parent gas molecules. This effect is particularly significant in the present work since a diffuse gas target was utilized throughout data taking. The most severe shifts in fragment kinetic energy occur when the velocity vector of the parent molecule points towards or away from the detector. These worst cases are considered in the following analysis.

The kinetic energy of the fragment due to dissociation is given by

\[ W_B = \frac{1}{2} M_B v^2 \quad (18) \]
where $V$ is the fragment's velocity with respect to the centre of mass of the molecule. Simple differentiation of this equation gives the change in fragment kinetic energy due to a small change in fragment velocity. The resulting equation is as follows:

$$\Delta w_B = M_B V \Delta V .$$  \hspace{1cm} (19)

If the parent molecule happens to be travelling towards the detector when the dissociation takes place, then the measured fragment velocity is actually $(V + \Delta V)$, where $\Delta V$ is the thermal velocity of the parent molecule. Thus it is possible to express Eq. (19) in the following way:

$$\Delta w_B = 2 \left[ \frac{w_B w_T M_B}{M} \right]^{1/2}$$ \hspace{1cm} (20)

In this equation, $M$ is the mass of the parent molecule and $w_T$ is its thermal kinetic energy. However, since there is no preferred direction of molecular motion, the kinetic energy uncertainty expressed in Eq. (20) must be an upper limit for the uncertainty due to this effect. In fact, it is likely that the majority of fragments have a kinetic energy uncertainty of about half this value. If this is the case, the fractional kinetic energy uncertainty, due to thermal motion of the target gas molecules, is given by

$$\frac{\Delta w_B}{w_B} = \left[ \frac{w_T M_B}{w_B M} \right]^{1/2} .$$ \hspace{1cm} (21)

This equation can be somewhat simplified if the parent gas
molecules are homonuclear and diatomic. For this special case, the above equation reduces to

$$\frac{\Delta W_B}{W_B} = \left(\frac{W_T}{2W_B}\right)^{1/2}$$

(22)

At room temperature and for a typical fragment kinetic energy of 3 eV, Eq. (22) gives a 6% uncertainty in $W_B$. It is of interest to note that this uncertainty would be somewhat smaller if the fragment was produced during the dissociation of a heteronuclear molecule for which $M$ is greater than $2M_B$ [see Eq. (21)].

Momentum transfer effects and other experimental uncertainties have a negligible affect on the time-of-flight and kinetic energy resolutions.

3.7 Experimental Uncertainties - The Nett Effect

It is of interest to calculate the total uncertainty involved in determining the dissociation limit of a state producing metastable fragments. As pointed out above, the electron beam is expected to have an energy spread of about 1 eV (F.W.H.M.). Thus, at best, it is only possible to measure a dissociation threshold to within ± 0.5 eV. This corresponds to a 2% uncertainty in a 25 eV dissociation threshold. Unfortunately, a much greater uncertainty is involved in the calculated kinetic energy of the fragments. As pointed out above, this uncertainty involves a 12% contribution due to the use of a 10 µs electron pulse and a 10 µs time-of-flight window. In addition, the
thermal motion of parent gas molecules (assumed to be homonuclear and diatomic) introduces a further 6% uncertainty into the calculation. Thus, the uncertainty involved in determining the dissociation limit of the state is expected to be about 13%. A general expression for this total uncertainty is presented below.

\[
\frac{\Delta D'_{AB}}{D'_{AB}} = \left[ \left( \frac{2\Delta t}{t} \right)^2 + \frac{W_{T'B} M_B}{W_B M} + \left( \frac{0.5}{E_{APP}} \right)^2 \right]^{1/2}
\]  

(23)

In this equation \( D'_{AB} \) is the dissociation limit of the state and \( E_{APP} \) is the appearance potential of the metastable fragments.

The dissociation limit uncertainties quoted in this thesis were calculated using this equation. Where necessary, the uncertainties involved in geometrically locating dissociation thresholds, due to poor data statistics, were also included.
CHAPTER 4

THE RESULTS FOR NITROGEN
4.1 Introduction

The results presented in this chapter concern the metastable nitrogen atoms produced during the electron impact dissociation of molecular nitrogen. The time-of-flight and kinetic energy distributions of these fragments are described in detail and the results are discussed in the light of excitation function measurements. A comparison of the present results with the results of other workers is presented in the final section.

4.2 Description of the $N^*$ Results

4.2.1 $N^*$ Signal Intensity as a Function of Gas Pressure and Electron Current

A pressure run for the metastable nitrogen atoms produced during the dissociation of molecular nitrogen is shown in Fig. 20. The data was taken manually using the techniques outlined in subsection 3.4.2 of Chapter 3. The plot of $N^*$ signal intensity against gas pressure is seen to be linear for pressures below about $9.5 \times 10^{-4}$ torr.

The gas pressure used during time-of-flight data accumulation was $2 \times 10^{-4}$ torr and the gas pressure used during excitation function data accumulation was $7.5 \times 10^{-4}$ torr. Research grade nitrogen gas was used throughout these studies.

A plot of $N^*$ signal intensity against electron current is shown in Fig. 21. This plot is seen to be linear for electron currents below 39 $\mu$A. In general, a 28 $\mu$A electron current was used during data taking.
Fig. 21

Intensity (Arbitrary Units)

Pressure = 6 x 10^{-4} torr

Electron Current (μA)

○ Nitrogen
□ Carbon Dioxide
● Nitrous Oxide

Fig. 20

Intensity (Arbitrary Units)

Electron Current = 19 μA

Pressure (Torr)

Electron Current = 19 μA
4.2.2 Time-of-Flight and Kinetic Energy Distributions of N*

The N* time-of-flight spectra, which were obtained at different electron energies, are presented in Fig. 22. All the flight times quoted in the figure were measured with respect to the centre of the 3 μs (F.W.H.M.) electron pulse. For clarity a corresponding scale, showing the total released kinetic energy, is also presented. The data was accumulated by computer using the technique outlined in subsection 3.4.4 of Chapter 3. The Cu/Be detector was used during this data taking and the resulting spectra were smoothed once using a routine which averages three points in a 1:2:1 ratio.

At an electron energy of 31 eV a single broad peak is obtained in the fragment signal intensity. This peak reaches a maximum at a flight time of about 70 μs. However, at an electron energy of 35 eV it becomes clear that this broad peak is actually made up of two overlapping peaks. One of these reaches a maximum at 70 μs and the other reaches a maximum at about 94 μs. These peaks are numbered (2) and (1) respectively. The spectrum obtained at 35 eV also shows evidence of a third process. This process produces fragments with a higher kinetic energy. At 56 eV this third process dominates the time-of-flight spectrum and thus obscures the peak due to process number (2). Process number (2) is, however, responsible for the long tail of peak number (3). The peak due to process number (1) is still visible at long flight times and the peak due to process number (3) reaches a maximum at about 60 μs. At higher electron
energies a fourth process produces a peak which reaches a maximum at about 45 $\mu$s.

It is of interest to transform the above time-of-flight spectra into corresponding kinetic energy distributions. In such distributions the fragment signal intensity is plotted against the total kinetic energy released during molecular dissociation. The necessary transformation, which is considered in Appendix 2, was performed by computer. The results of this transformation are presented in Fig. 23.

It can be seen from this figure that the four features of Fig. 22 are clearly resolved in the transformed spectra. In particular, the spectrum at 56 eV is of interest since it clearly shows features (1), (2) and (3). At first sight this seems rather a surprising result since only features (1) and (3) are clearly seen in the corresponding time-of-flight spectrum. This paradox can be explained by consideration of the transformation involved. This transformation strongly weights any signal arriving at long flight times. Thus, the long tail of the time-of-flight spectrum, at 56 eV, is seen as a distinct peak in the transformed spectrum. As pointed out above, this long time-of-flight tail is due to signal from process number (2).

The above discussion demonstrates the importance of transforming a time-of-flight spectrum into its corresponding kinetic energy distribution. However, since the transformation strongly weights signal arriving at long flight times, a certain amount of care is needed when interpreting the data. For
Fig. 23
example, a few background counts at long flight times may produce a steep rise at the low energy side of the transformed spectrum. It is thus essential, when interpreting results, to carefully examine both the transformed data and the time-of-flight data.

4.2.3 Photon Contamination of the N* Time-of-Flight Distributions

The time-of-flight spectra shown in Fig. 22 are contaminated at short times by what appears to be an exponential decay. In order to investigate this feature in detail, a 15 µs time-of-flight window was centred at a flight time of 20 µs. The signal arriving within this window was then plotted as a function of electron energy. The excitation function obtained is shown in Fig. 24. The data was accumulated on a multichannel scaler using the techniques outlined in subsection 3.4.5 of Chapter 3. The excitation function is seen to rise quite sharply from an excitation threshold of 8.5 ± 0.5 eV. It continues to rise in this way until a maximum is reached at about 17 eV. At higher electron energies the signal is seen to fall away.

The excitation threshold and general shape of this excitation function immediately suggests that the recorded signal is associated with the $^1\text{Π}_g$ state of molecular nitrogen. This state is metastable and has a reported lifetime of 115 ± 20 µs (Borst, 1970). This lifetime is significantly shorter than
Fig. 24

An excitation function for the photons observed in the N\textsuperscript{h} time-of-flight spectra
the time taken by the molecules to reach the detector and thus radiative decay may occur on the flight path. It is the photons produced during this radiative decay that are responsible for the decay curve seen at short flight times. This signal is seen to decay with time since only a finite number of molecules are excited to the $a^1\Pi_g$ state during each electron pulse.

An estimate of the lifetime of this state was made by fitting a known function to the observed decay. In order to obtain a suitable function for this purpose it was necessary to consider any signal losses caused by diffusion of the excited molecules. The simple model used for this purpose is considered in Appendix 3. From these considerations the following photon decay function was obtained:

$$I = I_o \left( \frac{1}{t^2} + C \right) e^{-\frac{t}{\tau}}$$  \hspace{1cm} (24)

In this expression the lifetime of the state is $\tau$, the decay time is $t$ and $C$ is a constant.

This decay function fits the observed photon decay extremely well if a lifetime of 130 $\mu$s is assumed. This value is in good agreement with the value quoted above. The theoretical and observed decay curves are shown in Fig. 25. To emphasize the importance of molecular diffusion in these considerations, a simple exponential decay is also presented. This decay has a time constant of 130 $\mu$s.
Observed Decay
\[ I = I_0 \left( \frac{1}{t_2 + c} \right) e^{-\frac{t}{\tau}} \]
\[ I = I_0 e^{-\frac{t}{\tau}} \]
\[ \tau = 130 \, \mu s \]
4.2.4 $N^*$ Excitation Functions

The $N^*$ excitation functions shown in Fig. 26 are of rather poor quality due to the very low signal intensities encountered during data taking. Despite this fact, the curves shown in the figure clearly show the onsets of processes (1), (2), (3) and (4) at the electron energies quoted. The average kinetic energy of the fragments, recorded in each of these plots, is also quoted in the figure. A 10 $\mu$s electron pulse and a 10 $\mu$s time-of-flight window was used during this data taking and the resulting signal was recorded on a multichannel scaler. In addition to the expected kinetic energy uncertainties, an estimate of the uncertainty involved in locating each of the above dissociation thresholds, is quoted in the figure.

The dissociation limits of processes (1), (2), (3) and (4), calculated from the above dissociation thresholds, are presented and discussed in the following section.

4.3 Discussion of the $N^*$ Results

The calculated dissociation limits of processes (1), (2), (3) and (4) are $24 \pm 3$ eV, $26 \pm 4$ eV, $35 \pm 5$ eV and $35 \pm 6$ eV respectively. These dissociation limits correspond fairly well to the dissociation limits of a number of $N_2^+$ molecular states. The dissociation limits of these molecular states are compared with the present results in Table 3. This observation immediately suggests that the four processes involve the
(Freund, 1973)

$47 \pm 1 \text{ eV}$

(Released K.E. = $12 \pm 2 \text{ eV}$)

$33 \pm 1 \text{ eV}$

(Released K.E. = $7 \pm 1 \text{ eV}$)

$30 \pm 1 \text{ eV}$

(Released K.E. = $6 \pm 0.8 \text{ eV}$)

Fragment K.E. = $0.5 \times$ Released K.E.

Electron Energy (eV) →

Fig. 26
excitation of high-Rydberg molecular states. Atoms in high-Rydberg states are produced during the dissociation of these molecules. The core-ion model for such a dissociation process is now discussed in detail.

A high-Rydberg state in an atom or molecule is a state which possesses such a large principle quantum number that the average distance \(\langle r \rangle\), from the nucleus to the electron, is large. In such a case, the core ion of the atom or molecule can be approximated to a point charge and thus the high-Rydberg electron behaves in a similar way to a hydrogenic electron. The orbital of such a high-Rydberg electron must be almost completely nonbonding. Consequently, the energy of the molecule, as a function of its internuclear distance, is given by the electronic states of the core ion, lowered only by the very small binding energy of the high-Rydberg electron. Potential energy curves of the high-Rydberg molecule are thus parallel to those of the core ion and lie less than 0.1 eV lower in energy. The model therefore predicts that the dissociation of a high-Rydberg molecule is governed entirely by the potential energy curves of the core ion. This remains the case until the distance between the separating nuclei becomes comparable to \(\langle r \rangle\). Until this time, the Rydberg electron has merely been a spectator to the dissociation process. As the nuclei separate, it is hypothesized that the Rydberg electron is most likely to remain bound to the ionic dissociation fragment in a high-Rydberg orbital. The kinetic energy of this high-Rydberg atom is,
<table>
<thead>
<tr>
<th>Fragments Produced</th>
<th>N$_2^+$ Diss. Limits (eV)</th>
<th>Process No.</th>
<th>Measured Diss. Limit (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$^+$(3P)$_{HR}$ + N$(4S)$</td>
<td>24.29</td>
<td>(1)</td>
<td>24 ± 3</td>
</tr>
<tr>
<td>&quot; + N$(2D)$</td>
<td>26.68</td>
<td>(2)</td>
<td>26 ± 4</td>
</tr>
<tr>
<td>&quot; + N$(2P)$</td>
<td>27.87</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot; + N$(3s^4P)$</td>
<td>34.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot; + N$(3s^2P)$</td>
<td>34.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot; + N$(3p^2S)$</td>
<td>35.89</td>
<td>(3) and (4)</td>
<td>35 ± 5</td>
</tr>
<tr>
<td>&quot; + N$^+$(3P)</td>
<td>38.83</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fragments Produced</th>
<th>N$_2^+$ Diss. Limits (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$^+$(3D)$_{HR}$ + N$(4S)$</td>
<td>35.73</td>
</tr>
<tr>
<td>&quot; + N$(2D)$</td>
<td>38.11</td>
</tr>
<tr>
<td>&quot; + N$(2P)$</td>
<td>39.30</td>
</tr>
</tbody>
</table>

**TABLE 3**

The results for nitrogen—a comparison of the present dissociation limits with the dissociation limits of a number of N$_2^+$ states (Freund, 1973).
however, the kinetic energy acquired by the atomic ion during dissociation of the molecular core ion. The Rydberg's electron's mass and binding energy have little effect on this dissociation process.

In general, the high-Rydberg fragments detected in a time-of-flight experiment will have ground state ionic cores since the fragments possessing excited cores are likely to autoionize before they reach the detector.

As shown in Table 3, the dissociation limit of process number (1) corresponds fairly well to the dissociation limit of a high-Rydberg molecule. Upon dissociation, this molecule breaks up into a ground state Nitrogen atom [i.e. N(4S)] and a high-Rydberg atom with a ground state ionic core (i.e. N\(^{+}(3P)HR\)). Therefore, since the ground state fragment cannot be detected in this experiment, the recorded signal must be due to the detection of high-Rydberg fragments.

In a similar way, the dissociation limit of process number (2) corresponds to the dissociation limit of a process which involves the production of a metastable Nitrogen atom [i.e. N(2D)] and a high-Rydberg atom with a ground state ionic core (i.e. N\(^{+}(3P)HR\)). Unfortunately, the uncertainty involved in calculating the dissociation limit of this process significantly overlaps the dissociation limit of a second process. This second process also involves the production of both metastable Nitrogen atoms and high-Rydberg atoms (i.e. N(2P) and N\(^{+}(3P)HR\) respectively). Thus it is not possible, from these
measurements alone, to positively identify the process responsible for peak number (2). Similarly, it is not possible to rule out the participation of both these processes during the data taking. However, it is possible to say with some certainty that the recorded signal is that of the high-Rydberg fragments and not that of the metastable fragments, since neither of the metastable fragments has sufficient excitation energy to eject electrons from the Cu/Be detector.

The measured dissociation limits of processes (3) and (4) are indistinguishable and correspond to the dissociation limits of several processes which involve the production of $N^+ (^3P)$HR fragments (see Table 3). Each of these processes also involves the production of a second Rydberg fragment. The dissociation limits of these processes and the fragment states produced are shown in Table 3. This table also shows the dissociation limits of several processes which involve the production of $N^+ (^3D)$HR fragments. The dissociation limits of these processes also lie fairly close to the measured dissociation limits. (N.B. These processes are included since rapid radiative decay of this fragment may compete with its autoionization and thus result in the production of $N^+ (^3P)$HR fragments.)

It is likely that high-Rydberg fragments, from a number of the above processes, are responsible for the peaks labelled number (3) and number (4). Unfortunately, limited apparatus resolution prevented a more detailed study of these contributing processes. However, the fact that two distinct peaks are
produced by these fragments, does suggest that the potential energy curve of at least one of these processes is fairly repulsive within the Franck-Condon region [i.e. the potential energy curve of the process or processes responsible for peak number (4)].

As a further check on the validity of the above arguments, the kinetic energy distributions of the fragments, observed in this experiment, have been compared with the corresponding dissociative ionization results of Kieffer and Van Brunt (Kieffer, 1967). The results of this comparison are shown in Fig. 27. If the above arguments are correct (i.e. if the detected fragments are produced during the dissociation of high-Rydberg molecules), then all the peaks obtained in the high-Rydberg curves should also appear in the corresponding $N^+$ spectra. Furthermore, the two sets of spectra should agree in peak position. The results of Fig. 27 clearly confirm this expectation for processes (2), (3) and probably (4) despite the fact that the compared spectra were obtained at different electron energies. Unfortunately, there seems to be little evidence of process (1) in the data of Kieffer and Van Brunt. However, this discrepancy is not a serious problem since the apparatus of these two workers is known to discriminate against low energy ions.

It would be of interest to identify the molecular high-Rydberg states which are involved in the above dissociation processes. Unfortunately, this is not possible, since little information is available about the $N_2^+$ states which correlate with
the above dissociation limits. However, the fact that process number (2) is seen as a distinct peak in the excitation function data, does suggest that the excitation of at least one of these states involves a spin forbidden transition (i.e. the excitation involves a change in multiplicity).

4.4 Comparison of the N\textsuperscript{a} Results with Published Data

A number of workers have studied the electron impact dissociation of N\textsubscript{2} and have reported the production of nitrogen atoms in high-Rydberg states. The most detailed of these investigations was performed by Smyth and Freund (Freund, 1973). The N\textsuperscript{a} results reported in this thesis are in excellent agreement with the results of these two workers. To emphasize this agreement, some of the kinetic energy distributions obtained by these workers are plotted with the present results in Fig. 28. This comparison clearly shows that the two sets of distributions agree in both general shape and peak position. The corresponding time-of-flight spectra, obtained by Smyth and Freund, are shown in Fig. 29. This data may also be directly compared with the time-of-flight data obtained in the present experiment (see Fig. 22). However, the flight times quoted in the figures cannot be directly compared since the experimental flight paths were of different lengths. The flight path used in this experiment is approximately twice as long as the flight path
Fig. 28
used by Smyth and Freund. Thus it is necessary, when comparing the two sets of data, to halve the flight times quoted in Fig. 22.

The excitation functions obtained by Smyth and Freund are of somewhat better quality than the excitation functions obtained in the present experiment. For comparison, these excitation functions are presented in Fig. 26 (see insert). During this data taking, Smyth and Freund were able to use a fairly narrow electron pulse and a fairly narrow time-of-flight window. Thus they were able to accurately determine the dissociation limits of processes (1), (2), (3) and (4). The use of a gas beam, during this data taking, further reduced the experimental uncertainties. Generally, the dissociation limits obtained by Smyth and Freund are in good agreement with the results obtained in this experiment. However, the results obtained by these workers clearly demonstrate that only one process is responsible for the peak labelled number (2). The dissociation limit of this process corresponds to the production of an $N(2D)$ atom and an $N^+(3P)$HR fragment. In addition, Smyth and Freund were able to clearly demonstrate that this process involves a spin forbidden transition. This result is in agreement with the suggestions of Section 4.3. Finally, the fact that Smyth and Freund used a special high-Rydberg detector throughout data taking suggests that the arguments of Section 4.3 are correct. The apparatus used by these workers has been briefly described in subsection 2.3.1 of Chapter 2.
Fig. 29 (Freund, 1973)
CHAPTER 5

THE RESULTS FOR CARBON DIOXIDE
5.1 Introduction

The results presented in this chapter are concerned with the fast metastable fragments produced during the electron impact dissociation of Carbon Dioxide. The time-of-flight and kinetic energy distributions of these fragments are described in detail and the results are discussed in the light of excitation function measurements. In the final section, the present results are compared with the results of other workers.

5.2 Description of the Fast Fragment Results

5.2.1 Signal Intensity of the Fast Fragments as a Function of Gas Pressure and Electron Current

A pressure run for the fast metastable fragments produced during the molecular dissociation of CO$_2$ is shown in Fig. 20. This data was taken manually using the techniques discussed above. The plot is seen to be linear for pressures below about 9 x 10^{-4} torr. The gas pressure used during time-of-flight data accumulation was 4 x 10^{-4} torr. Research grade CO$_2$ was used throughout these studies.

A similar plot of this signal intensity against electron current is shown in Fig. 21. This plot is seen to be linear for electron currents below about 34 $\mu$A. In general, a 22 $\mu$A electron current was used during data taking.
5.2.2 Time-of-Flight and Kinetic Energy Distributions of the Fast Fragments

The fast fragment time-of-flight spectra, which were obtained at different electron energies, are presented in Fig. 30. All the flight times quoted in the figure were measured with respect to the centre of the 10 μs (F.W.H.M.) electron pulse. The data was accumulated by computer using the techniques described above. The low work-function detector was used during this data taking. The resulting spectra are presented unsmoothed.

At an electron energy of 20 eV there is little evidence of a fast peak in the time-of-flight data. However, at an electron energy of 30 eV a fast peak is clearly seen. This peak is labelled number (1). By the time the electron energy has reached 40 eV there is clear evidence of a second process producing faster fragments. However, at an electron energy of 50 eV, there is some evidence to suggest that this faster peak is actually made up of two overlapping peaks. Unfortunately, the fast growth of the peak labelled number (3) tends to obscure any peak due to process number (2). Process number (2) is, however, responsible for the long tail of peak number (3). This long tail is seen to obscure the peak due to process number (1). By the time the electron energy has reached 75 eV there is clear evidence of a fourth process producing even faster fragments. At this electron energy, a small peak due to process number (1) is also visible. The spectrum obtained at 100 eV is similar to the spectrum obtained at 75 eV. All the spectra shown in Fig. 30
clearly show the presence of a much broader peak at longer flight times.

Some of the kinetic energy distributions, corresponding to the fast peaks of the time-of-flight distributions, are shown in Fig. 31. In performing this transformation it was assumed that the detected fragment was in all cases an oxygen atom. The validity of this assumption is discussed in section 5.3. The kinetic energies quoted in the figure are based on this assumption and refer only to this detected fragment.

Unfortunately, it was not possible to calculate the total kinetic energy released during the dissociation since a number of the dissociation processes may well involve the total fragmentation of the CO₂ molecule (i.e. the production of three dissociation fragments).

It can be seen from Fig. 31 that the four features of Fig. 30 are clearly resolved in the transformed spectra. In particular, the tiny bump due to process number (2) is of interest since little evidence of its existence is available in the corresponding time-of-flight data. The fact that this little bump appears in almost all the transformed distributions compensates for its modest dimensions.

5.2.3 The Fast Fragment Excitation Functions

The fast fragment excitation functions shown in Fig. 32 clearly show the onsets of processes (1), (2), (3) and (4) at
Fig. 31

Signal Intensity (Arbitrary Units)

Fragment Kinetic Energy (eV)
the electron energies quoted. The average kinetic energy of the fragments (assumed to be oxygen atoms) recorded in each of these plots, is also quoted in the figure. A 10µs electron pulse and a 10µs time-of-flight window was used during this data taking and the resulting signal was recorded on a multichannel scaler. The kinetic energy uncertainties, quoted in the figure, were calculated in accordance with the discussions of Chapter 3.

Where possible, the dissociation limits of the various processes were also calculated. The dissociation limits of these processes are presented and discussed in the following section.

5.3 Discussion of the Fast Fragment Results

In order to calculate the dissociation limits of the processes it is first necessary to identify the detected fragment. This is a fairly easy task at low electron energies since three-fragment dissociation processes can then be excluded. At such electron energies, a linear CO₂ molecule is likely to dissociate into a fast oxygen atom and a slow Carbon Monoxide fragment. (N.B. In order to liberate a carbon atom it is necessary to supply sufficient energy to break four covalent bonds.) In such a situation, the fast-fragment time-of-flight peaks must be due to the detection of metastable oxygen atoms. It is likely that processes (1) and (2) are of this type, since the thresholds of these processes lie below the
Fig. 32

Electron Energy (eV) →

- 0 Signal Intensity (Arbitrary Units)

K.E. = 6 ± 0.9 eV

K.E. = 2 ± 0.2 eV

K.E. = 1.4 ± 0.2 eV

25 ± 0.5 eV

34 ± 0.5 eV

46 ± 0.5 eV

(1)

(2)

(3)

(4)
energy required to produce a fast metastable fragment via a total fragmentation process. For example, the minimum electron energy required to completely dissociate a CO$_2$ molecule and produce a detectable carbon atom is 27.6 eV (Misakian, 1975). Similarly, the minimum electron energy required to completely dissociate a CO$_2$ molecule and produce a detectable oxygen atom [O($^5\text{S}^0$)] is 25.7 eV. (N.B. O($^1\text{S}$) and O($^1\text{D}$) fragments were not detectable during this work.) Both these electron energies are somewhat higher than the measured dissociation thresholds of processes (1) and (2). It therefore follows that processes (1) and (2) involve the production of only two dissociation fragments and that the faster of these fragments is a metastable oxygen atom.

Unfortunately, the dissociation limits of these processes are still somewhat uncertain since it is now possible to produce vibrationally excited fragments. However, if it is assumed that the CO fragments, produced during processes (1) and (2), are in the ground vibrational state then an upper limit for the dissociation limits of these processes can be calculated. These upper limits are $20 \pm 2$ eV and $22 \pm 2$ eV for processes (1) and (2), respectively.

The above dissociation limits correspond to a number of possible processes which involve the production of a detectable oxygen atom and an electronically excited carbon monoxide fragment. These processes are presented with their respective dissociation limits (assuming no vibrational excitation) in Table 4. A number
Process number (1) Measured dissociation limit = 20 ± 2 eV

<table>
<thead>
<tr>
<th>Fragments Produced</th>
<th>Diss. Limit (eV)</th>
<th>Parent State</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) CO(a^3π) + O(5S^0)</td>
<td>20.6</td>
<td>π</td>
<td>Dipole Allowed Transition</td>
</tr>
<tr>
<td>(b) CO(a^1Σ^+) + O(5S^0)</td>
<td>21.5</td>
<td>Σ^-</td>
<td>&quot; Forbidden &quot;</td>
</tr>
<tr>
<td>(c) CO(a^3π) + O(5P) - O(5S^0)</td>
<td>21.7</td>
<td>Σ^+, Σ^-, π, Δ</td>
<td>&quot; Allowed &quot;</td>
</tr>
<tr>
<td>(d) CO(X^1Σ^+) + O(HR)</td>
<td>19.0</td>
<td>Σ^-, π, Δ</td>
<td>&quot; Allowed &quot;</td>
</tr>
</tbody>
</table>

Process number (2) Measured dissociation limit = 22 ± 2 eV

<table>
<thead>
<tr>
<th>Fragments Produced</th>
<th>Diss. Limit (eV)</th>
<th>Parent State</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(e) CO(a^1Σ^+) + O(5S^0)</td>
<td>21.5</td>
<td>Σ^-</td>
<td>Dipole Forbidden Transition</td>
</tr>
<tr>
<td>(f) CO(d^3Δ) + O(5S^0)</td>
<td>22.1</td>
<td>Δ</td>
<td>&quot; Forbidden &quot;</td>
</tr>
<tr>
<td>(g) CO(e^3Σ^-) + O(5S^0)</td>
<td>22.5</td>
<td>Σ^+</td>
<td>&quot; Allowed &quot;</td>
</tr>
<tr>
<td>(h) CO(a^3π) + O(5P) - O(5S^0)</td>
<td>21.7</td>
<td>Σ^+, Σ^-, π, Δ</td>
<td>&quot; Allowed &quot;</td>
</tr>
<tr>
<td>(i) CO(a^1Σ^+) + O(5P) - O(5S^0)</td>
<td>22.6</td>
<td>Σ^-, π</td>
<td>&quot; Allowed &quot;</td>
</tr>
<tr>
<td>(j) CO(d^3Δ) + O(5P) - O(5S^0)</td>
<td>23.2</td>
<td>π, Δ, Σ^-</td>
<td>&quot; Allowed &quot;</td>
</tr>
<tr>
<td>(k) CO(e^3Σ^-) + O(5P) - O(5S^0)</td>
<td>23.6</td>
<td>Σ^+, π</td>
<td>&quot; Allowed &quot;</td>
</tr>
</tbody>
</table>

TABLE 4

The results for carbon dioxide - a comparison of the present dissociation limits with the dissociation limits of a number of possible processes (Freund, 1971).
of possible molecular parent states, which may be excited during these processes, are also presented in the table. These molecular parent states were obtained by applying correlation rules to the respective dissociation processes (Herzberg, 1967). Using this information, it is possible to argue against the participation of some of the listed processes. For example, transitions between a \( \Sigma^+ \) state (ground state \( \text{CO}_2 \)) and a \( \Sigma^- \) state are dipole forbidden and are, therefore, unlikely to be observed. In addition, the excitation function of such a process should be peaked at low electron energies. The excitation functions shown in Fig. 32 do not exhibit this behaviour and thus the participation of such a process can be excluded. This kind of argument has been applied to the processes listed in Table 4 and where necessary, an appropriate comment has been made.

As shown in Table 4, there are only three possible processes which correlate with the measured dissociation limit of process number (1). These processes are labelled (a), (c) and (d). It is of interest to note that two of these processes result in the production of a metastable carbon monoxide fragment \([\text{CO}(a^3 \Pi)]\) and a metastable oxygen atom \([O(5\Sigma^0)]\). Process (a) produces these fragments directly and process (c) produces them via a cascade mechanism. The third process results in the production of a ground state carbon monoxide fragment \([\text{CO}(X^1 \Sigma_g^-)]\) and an oxygen atom in a Rydberg state. Unfortunately, at the present time, it is not possible to say which of these processes is responsible for feature number (1). However, excitation
function studies of the carbon monoxide fragments, produced during the electron impact dissociation of CO$_2$ have shown the presence of a process onset at about 21 eV (Freund, 1971).

Freund has suggested that this increase in signal is due to the detection of a$^3\Pi$ fragments and that process (a) is a possible contender. (N.B. The slow time-of-flight peak, recorded in the present experiment, is probably due to the detection of CO(a$^3\Pi$) fragments.) The above suggestion is in good agreement with the present results although it is not possible to totally rule out the participation of process (c). (N.B. Process (c) also involves the production of CO(a$^3\Pi$) fragments.) Furthermore, additional evidence for the participation of process (c) comes from the angular distribution studies of feature (1) (Misakian, 1975). These studies suggest that the molecular parent state, involved in the dissociation process, has $\Sigma_u^+$ symmetry. This result suggests that process (c) is a more likely contender than process (a) since process (a) involves the excitation of a $\Pi$ state. This evidence must, however, be considered cautiously since the measured dissociation limit of process (1) compares more favourably with process (a) than with process (c) (see Table 4): To account for this apparent inconsistency, Misakian has suggested that the initial excitation is to a $\Sigma_u^+$ state and that this state is predissociated by a nearby $\Pi_u^+$ state.

Of the three processes, process (d) is probably the most unlikely contender since this process does not provide the required a$^3\Pi$ carbon monoxide fragments. Furthermore, the
molecular parent state of this process will not be a $\Sigma_u^+$ state.

As shown in Table 4, there are three possible processes which correlate with the measured dissociation limit of process number (2). These processes are labelled (g), (h) and (k). (N.B. Processes (i) and (j) are not included since these processes do not involve the excitation of a $\Sigma^+$ state (see below).)

It is of interest to note that two of these processes [i.e. processes (g) and (k)] result in the production of a Carbon Monoxide fragment in the $e_3^3\Sigma^-$ state and an oxygen atom in the $^5S_0$ state. Process (g) produces these fragments directly and process (k) produces them via a cascade mechanism. The third process also involves a cascade mechanism. This process involves the production of a metastable Carbon Monoxide fragment [CO($a^3\Pi$)] and a metastable Oxygen atom [O($^5S_0$)]. This process has been discussed above since it possibly participates in the production of feature (1).

Misakian has performed angular distribution studies of feature (2) and has suggested that the molecular parent state, involved in the dissociation process has $\Sigma_u^+$ symmetry. This result presents evidence for the exclusion of processes (e), (f), (i) and (j).

Of the three possible processes, the dissociation limit of process (h) correlates most nearly with the measured dissociation limit of feature (2). Therefore, since it is unlikely that this process is responsible for the production of feature (1) and feature (2), it is tempting to suggest that this process is responsible for feature (2) and that it does not participate in
the production of feature (1) at all. Unfortunately, the dissociation limit of process (g) also compares favourably with the measured dissociation limit of process (2). Therefore, it is not possible to totally rule out the participation of this process.

Of the three processes, process (k) is probably the least likely to be responsible for the production of feature (2) since the dissociation limit of this process is 1.6 eV above the measured dissociation limit.

Unfortunately, it is not possible to calculate with certainty the dissociation limits of processes (3) and (4) since the dissociation thresholds of these processes lie far above the energy required to totally fragment the CO₂ molecule during the production of a detectable fragment (i.e. the processes may well involve the production of three dissociation fragments). However, if it is assumed that both processes involve a two-fragment dissociation and that the detected fragment is an oxygen atom then the dissociation limits of processes (3) and (4) are 25 ± 4 eV and 37 ± 6 eV respectively. It is of interest to note that the above dissociation limit for process (3) correlates fairly well with the dissociation limit of a process which involves the production of Rydberg oxygen atoms. This process has a dissociation limit of about 25 eV and also involves the production CO(a^3π) fragments.
5.4 Comparison of the Fast Fragment Results with the Results of Other Workers

As pointed out above, the fast fragments produced during the electron impact dissociation of CO₂ have been studied by Misakian and Mumma (Misakian, 1975). The results obtained in the present experiment are in good agreement with the results of these two workers. To emphasize this agreement, the kinetic energy distributions, obtained by these workers are plotted with the present results in Fig. 33. Despite a small displacement in kinetic energy, this comparison clearly shows that the distributions agree in general shape and that four processes are present in both sets of data.

Misakian and Mumma have studied these processes in detail and have shown the presence of a fifth peak which strongly overlaps the peak due to process number (4). This feature was discovered as a result of angular distribution and excitation functions measurements.

In general, the excitation functions obtained by Misakian and Mumma are of rather poor quality. These excitation functions do not exhibit sharp onsets and thus the dissociation limits, quoted by these workers are somewhat questionable. In addition, their method of analysis seems somewhat suspect since they preferentially compensate for the dissociation of molecules which are travelling towards the detector. Their resulting dissociation limits are therefore somewhat higher than the dissociation limits calculated in
Figure 33

Fragment Kinetic Energy (eV)

0 Signal Intensity (Arbitrary Units)

Misakian and Mumma

Present Results

100 eV

75 eV

50 eV

40 eV

30 eV

(1) (2) (3) (4)
the present work. In particular, they suggest that process (2) has a dissociation limit of about 25 eV. This dissociation limit is about 3 eV greater than the present suggested value. In accordance with this dissociation limit, Misakian and Mumma suggest that this process involves the production of Rydberg Oxygen atoms. However, the present results suggest that this assignment is incorrect.

Despite the above uncertainties, Misakian and Mumma suggest that the dissociation limit of process number (1) is about 20 eV and that this process involves the production of a CO($a^3\Pi$) fragment and a $5\Sigma^0$ Oxygen atom. This suggestion is in good agreement with the present results.

In addition to studying the angular distributions of fragments produced during processes (1) and (2), Misakian and Mumma have performed angular studies on features (4) and (5). They suggest that the angular distributions of these features [i.e. features (4) and (5)] are most easily interpreted by assuming that the parent molecules are excited to a $\Pi_u$ state and a $\Sigma_u$ state respectively and that these molecules remain linear throughout the dissociation. If this is the case, they further suggest that features (4) and (5) are due to the detection of Oxygen atoms (possibly in Rydberg states). Using a special high-Rydberg detector, Freund (Freund, 1971) has performed a preliminary investigation of the composite fast peak and has reported the production of such fragments.
CHAPTER 6

THE RESULTS FOR NITROUS OXIDE
6.1 Introduction

The preliminary results presented in this chapter are concerned with the fast metastable fragments produced during the electron impact dissociation of Nitrous Oxide. Preliminary time-of-flight distributions are presented and the results are discussed in the light of published data.

Unfortunately, an excitation function study of these fragments is not available at this time.

6.2 Description of the Fast Fragment Results

6.2.1 The Signal Intensity of the Fast Fragments as a Function of Gas Pressure and Electron Current

A pressure run for the fast metastable fragments produced during the molecular dissociation of N₂O is shown in Fig. 20. This data was taken manually using the techniques discussed above. The plot is seen to be linear for pressures below about 8 x 10⁻⁴ torr.

The gas pressure used during time-of-flight data accumulation was 4 x 10⁻⁴ torr.

A similar plot of this signal intensity against electron current is shown in Fig. 21. This plot is seen to be linear for electron currents below 35 μA. In general, a 22 μA electron current was used during data taking.

6.2.2 Time-of-Flight Distributions of the Fast Fragments

The fast fragment time-of-flight spectra, which were
obtained at electron energies of 50 eV and 100 eV, are presented in Fig. 34. All the flight times quoted in the figure were measured with respect to the centre of the 3 μs (F.W.H.M.) electron pulse. The data was accumulated by computer using the techniques described above. The low work-function detector was used during this data taking and the resulting spectra were smoothed once.

At an electron energy of 50 eV a single fast peak is seen in the time-of-flight data. This peak is labelled number (1). However, by the time the electron energy has reached 100 eV there is clear evidence of a second process which produces faster fragments. The peak due to this process is labelled number (2). In addition, both of the time-of-flight distributions shown in Fig. 34 clearly show the presence of a much broader peak at longer flight times.

The approximate kinetic energies of the fragments produced by processes (1) and (2) are indicated in the figure. In performing this calculation it was assumed that the detected fragment was in all cases an oxygen atom. The validity of this assumption is discussed in the next section.

Below an electron energy of 20 eV there is little evidence of the fast peaks of Fig. 34. However, as the electron energy continues to drop, the broad peak of Fig. 34 shifts to longer flight times. This shift eventually exposes a tiny peak at a flight time of about 83 μs. The resulting time-of-flight spectrum, obtained at 10 eV, is shown in Fig. 35. The figure
compares the relative heights of both peaks and also shows the small peak on an expanded scale. Despite the modest dimensions of the small peak (about 60 times the background), repeated data taking yielded results similar to those shown in the figure. The approximate kinetic energy of the fragments responsible for this peak is quoted in the figure.

6.2 Discussion and Comparison of the Fast Fragment Results

Gilpin and Welge (Gilpin, 1971) have studied the photodissociation of N\textsubscript{2}O in the vacuum ultraviolet and have reported the detection of O\(^{1}\text{S}\) metastable oxygen atoms. They report that the time-of-flight peak, caused by these fragments, reaches a maximum at a kinetic energy of about 1.9 eV. This result is in excellent agreement with the results shown in Fig. 35. Thus it is likely that the small fast peak obtained at an electron energy of 10 eV is due to the detection of O\(^{1}\text{S}\) oxygen atoms.

In addition to the detection of O\(^{1}\text{S}\), Gilpin and Welge have reported the presence of a much broader peak at longer flight times. They suggest that this peak is due to the detection of nitrogen molecules in the A\(^{3}\text{E}^\text{u}\) state. In a similar way, it is likely that the broad peaks of Fig. 34 are due to the detection of these fragments. A short account of the experiment performed by Gilpin and Welge has been presented in subsection 2.3.3 of Chapter 2.

Unfortunately, little information is available about the
Fig. 35
fragments produced during the electron impact dissociation of $N_2O$. Thus it is difficult, in the absence of excitation function data, to identify the fragments responsible for the peaks shown in Fig. 34. However, it is possible that the fast peaks shown in this figure are also due to the detection of oxygen fragments.
CHAPTER 7

CONCLUSIONS
7.1 Summary and Conclusions

The fast metastable atoms produced during the molecular dissociation of $N_2$ and $CO_2$ have been studied by time-of-flight spectroscopy following excitation by electron impact. The dissociation limits of various molecular parent states have been calculated and the dissociation fragments identified. Nitrogen atoms in high-Rydberg states have been detected and the production of these fragments has been described in terms of the core-ion model for dissociation. In addition, the carbon dioxide studies have revealed the participation of two distinct processes which involve the production of $^{5}S^0$ oxygen atoms. It is likely that one of these processes involves a cascade mechanism. Of the two remaining processes, it is likely that at least one involves the production of a high-Rydberg oxygen atom.

Preliminary studies of the dissociation of $N_2O$ have revealed the participation of two distinct processes which involve the production of fast metastable fragments. At lower electron energies a third process has been observed. It is likely that this process involves the production of $^1S$ oxygen atoms.

7.2 Future Developments

The results presented in this thesis clearly demonstrate the versatility of the present experimental setup. However, in order to fully develop the potential of this experiment, it is
necessary to overcome a number of apparatus limitations. The most serious of these limitations is absence of some form of mass discrimination. The absence of such discrimination prevents the direct identification of fragment species when studying the dissociation of heteronuclear molecules. To partially overcome this problem it is proposed that a quadrupole mass spectrometer be incorporated in the present setup. Such an addition would enable the direct detection and identification of high-Rydberg fragments since these fragments are readily ionized by strong electric fields. Such a setup would enable high-Rydberg processes to be distinguished from those involving the production of other metastable fragments and would also enable a mass analysis to be performed on the high-Rydberg fragments. Unfortunately, it is difficult to perform a mass analysis on the remaining metastable fragments since these fragments are difficult to ionize.

A further limitation of the present apparatus concerns the difficulties involved in studying the angular distributions of dissociation fragments. As pointed out above, the detector system was found to be affected by rotation of the electron gun’s focusing magnet. In order to overcome this problem, it will be necessary to install suitable magnetic shielding in the apparatus.

A photon source has been designed and will be added to the apparatus in the near future in order to study the metastable fragments produced during the photodissociation of simple
molecules, particularly those of atmospheric interest. Initially, this photon source will consist of a rapidly pulsed continuum flash-lamp. However, it is hoped that in the near future sufficient funds will be available to enable the replacement of this source by a high intensity tunable laser.

In order to reduce the uncertainty in fragment kinetic energy, introduced by the thermal motion of parent gas molecules, a gas beam system will also be installed in the apparatus.

The technique currently being used to detect fragments in low lying metastable states will be developed and a number of new detection techniques investigated.

The present experimental setup is currently being used to study the dissociation of both linear and non-linear molecules of atmospheric interest. Molecules to be studied include CH₄, NH₃ and the freons.
APPENDIX 1

The time-of-flight slit function obtained by convoluting a 10 μs electron pulse with a 10 μs time-of-flight window, is triangular in shape and has a base width of 20 μs. This convolution process is shown schematically in Fig. 36 for perfectly shaped pulses of width T.

Consider the electron pulse to be made up of a large number of very narrow electron pulses of width ΔT. For electron pulse number (1), centred at t = 0, the recorded fragments have flight times which range from t to t + T. These fragments are represented by a rectangular box shown in the figure [i.e. box number (1)]. For an electron pulse centred at t = -ΔT [i.e. electron pulse number (2)], the recorded fragments have flight times which range from t + ΔT to t + ΔT + T. These fragments are represented by box number (2). In a similar way, the remaining electron pulses also produce fragments which have a range of flight times. These fragments are represented by the remaining rectangular boxes. The time-of-flight slit function simply represents the distribution of recorded fragments as a function of fragment time-of-flight and can be obtained by summing all the fragments which have flight times between t and t + dt. For the above case, the resulting distribution function is obviously triangular and has a base width of 2T.

It can be seen from Fig. 36 that the best estimate of the time-of-flight of the recorded fragments is t + T.
The time-of-flight slit function obtained by convoluting a rectangular electron pulse with a rectangular time-of-flight window.
APPENDIX 2

The total kinetic energy released during a two fragment dissociation process is given by

\[ W = \frac{M_{AB}}{M_A} w_B \]  \hspace{1cm} (25)

where \( w_B \) is the kinetic energy of fragment \( B'' \), \( M_{AB} \) is the mass of the molecule and \( M_A \) is the mass of fragment \( A' \).

The kinetic energy of fragment \( B'' \) can be calculated if its time of flight over a fixed distance is known. It thus follows that

\[ w_B = \frac{1}{2} M_B \frac{L^2}{t^2} \]  \hspace{1cm} (26)

where \( L \) is the length of the flight path and \( t \) is the fragment's flight time. However, in order to transform time-of-flight distributions into kinetic energy distributions, it is necessary to satisfy the following condition. Namely,

\[-F'(w_B)dw_B = F(t)dt \]  \hspace{1cm} (27)

where \( F(t) \) is the time-of-flight distribution function and \( F'(w_B) \) is the corresponding kinetic energy distribution function. This equation satisfies the necessary condition that the area under the transformed distribution curve must equal the area under the original time-of-flight distribution curve. This area represents the total number of fragments recorded during the experiment and must remain independent of the transformation.

Upon differentiating Equation (26) with respect to \( t \),
we obtain the following expression for $dW_B$. Namely,

$$dW_B = -\frac{M_B}{t^3} L^2 dt.$$  \hspace{1cm} (28)

This expression can now be substituted into Equation (27) in order to express the kinetic energy distribution function in terms of the known time-of-flight distribution function. It thus follows that

$$F'(W_B) = \frac{t^3 F(t)}{M_B L^2}.$$  \hspace{1cm} (29)

In a similar way,

$$F'(W) = \frac{M_A t^3 F(t)}{M_{AB} M_B L^2}$$  \hspace{1cm} (30)

where $F'(W)$ is the fragment distribution as a function of the total kinetic energy released during the dissociation process.

It is important to notice that these transformations involve a $t^3$ factor and thus strongly weight any signal arriving at long flight times.
APPENDIX 3

In order to obtain the decay function quoted in Equation (24), it is necessary to consider any signal losses caused by diffusion of the excited molecules. A number of these molecules drift out of the "line-of-sight" of the detector before radiating. As may be expected, the final form of this decay function is largely dependent on the apparatus geometry. Examination of this geometry shows that photons may only be detected if the decay occurs within a cone of apex angle $2\alpha$ (see Fig. 37). The apex of this cone lies at a distance $l$ from the source of the metastable molecules. (N.B. For this simple model it is assumed that the metastable molecules diffuse out from a point source.) The diffusion process is now considered in detail.

At time $t = 0$, $n$ metastable molecules are created at point $S$. These metastable molecules have a lifetime $\tau$ and a Maxwell-Boltzmann distribution of velocities. Of these molecules, the number having speeds between $v$ and $v + dv$ is $dn_v$. After time $t$, the $dn_v$ molecules are uniformly distributed in the elemental volume $4\pi(vt)^2 dv$. If $t$ is sufficiently large, only part of this volume still lies within the cone (see figure). For such a situation, the fractional volume seen by the detector is given by the following approximate relation.

$$\frac{\Delta V}{V} = \frac{2\pi(\tan^2 \alpha \cdot L^2 + v^2 L^2) t}{4\pi(vt)^2 t} dv$$  \hspace{1cm} (31)
Fig. 37
Photon signal losses due to molecular diffusion - the effect of the present apparatus geometry.
From this relation it follows that the number of metastable molecules with speeds between $v$ and $v + dv$, capable of producing a detectable photon, is given by

$$dn_v = \frac{1}{2} (\tan \frac{\nu}{2}) \left( \frac{L^2}{v^2 t^2} + 1 \right) dn_v.$$  \hspace{1cm} (32)

If $t$ is sufficiently large, this equation may be integrated over all $v$ in order to obtain the total number of metastable molecules capable of producing a detectable photon. This number is given by

$$n_d = K \left( \frac{L^2}{t^2} + \frac{kT}{M} \right).$$ \hspace{1cm} (33)

where $k$ is Boltzmann's constant, $M$ is the mass of the molecule, $T$ is the absolute temperature and $K$ is a constant. These molecules decay exponentially and thus the observed photon signal has the following form

$$I = I_o \left( \frac{1}{t^2} + C \right) e^{-\frac{t}{\tau}}.$$ \hspace{1cm} (34)

In this equation the constant $C$ is given by $kT/L^2M$ and for nitrogen molecules at room temperature has a value of about $8 \times 10^7$ sec$^{-2}$. The distance $L$, which is dependent on the present apparatus geometry, has a value of about 3.3 cm.

N.B. The above model assumes that decay of the $^1\Pi_g$ state may be represented by a single exponential decay function. Freund has pointed out that such an assumption is not strictly correct. (R.S. Freund, J. Chem. Phys. 56, 4344 (1972)).
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In the summer of 1972 I graduated from the University of York (England) with an honours degree in Physics. In January 1973 I began graduate work in Physics at the University of Windsor. During the course of this work I was the recipient of a University of Windsor Postgraduate Scholarship.