UNCONVENTIONAL PHOTOELECTRON SPECTROSCOPIC STUDIES:
PEPS OF SOME TRANSIENT SPECIES AND REACTIVE MOLECULES

by

SHUIT-TONG LEE
B.Sc., The Chinese University of Hong Kong, 1969
M.Sc., University of Rochester, New York, 1972

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
in the Department of
CHEMISTRY

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA
October, 1974
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Chemistry

The University of British Columbia
Vancouver 8, Canada

Date Oct. 9 1974
ABSTRACT

A fast pumping, versatile photoelectron spectrometer suitable for the study of transient species and reactive molecules has been designed, constructed and tested. The photoelectron spectra of seventeen such compounds (CS, SO, S\textsubscript{2}O, HN=NH, DN=ND, CH\textsubscript{3}H=NH, HCP, OCSe, SCSe, CSe\textsubscript{2}, O\textsubscript{3}, FNO, ClNO, BrNO, HNO\textsubscript{3}, ClNO\textsubscript{2} and FNO\textsubscript{2}) have been obtained. The individual spectra have been assigned by using information supplied from vibrational analysis, by comparison with molecular orbital calculations and with related molecules. The experimental Franck-Condon factors have been utilized to estimate the geometries of the ionic states, and the procedure has been found to be quite reliable. The study has shown the potential of photoelectron spectroscopy in providing information on the electronic structure of transient species and reactive molecules, information that is difficult to obtain by other spectroscopic techniques.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER I:</th>
<th>INTRODUCTION ..................................................</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHAPTER II:</td>
<td>THEORY OF PHOTOELECTRON SPECTROSCOPY .....................</td>
<td>6</td>
</tr>
<tr>
<td>2.1</td>
<td>Characteristic of a Photoelectron Spectrum ................</td>
<td>6</td>
</tr>
<tr>
<td>2.2</td>
<td>The Interpretation of Molecular PE Spectra ................</td>
<td>9</td>
</tr>
<tr>
<td>2.2.1</td>
<td>A Brief Survey of Assignment Criteria ....................</td>
<td>9</td>
</tr>
<tr>
<td>2.2.2</td>
<td>Koopmans' Theorem and the Calculation of Vertical IP's ...</td>
<td>12</td>
</tr>
<tr>
<td>(a)</td>
<td>Koopmans' Theorem and its Implications ...................</td>
<td>12</td>
</tr>
<tr>
<td>(b)</td>
<td>Application of Koopmans' Theorem in PES ..................</td>
<td>16</td>
</tr>
<tr>
<td>(c)</td>
<td>Other Methods for Calculating Vertical IP's ..............</td>
<td>18</td>
</tr>
<tr>
<td>(d)</td>
<td>Open Shell Molecules ........................................</td>
<td>19</td>
</tr>
<tr>
<td>2.2.3</td>
<td>Franck-Condon Principle in PES ............................</td>
<td>21</td>
</tr>
<tr>
<td>(a)</td>
<td>Wave Mechanical Formulation of the Franck-Condon (FC) Principle ..................</td>
<td>21</td>
</tr>
<tr>
<td>(b)</td>
<td>Qualitative Application of the FC Principle in PES ....</td>
<td>24</td>
</tr>
<tr>
<td>(c)</td>
<td>Quantitative Application of the FC Principle in PES ..........</td>
<td>26</td>
</tr>
<tr>
<td>2.2.4</td>
<td>Selection Rules in PES .......................................</td>
<td>33</td>
</tr>
<tr>
<td>(a)</td>
<td>Selection Rules in Electronic Excitations ..................</td>
<td>33</td>
</tr>
<tr>
<td>(b)</td>
<td>Selection Rules in Vibrational Excitations ..................</td>
<td>36</td>
</tr>
</tbody>
</table>
CHAPTER III: THE SPECTROMETER AND PERFORMANCE

3.1 Introduction ......................................................... 42

3.2 General Design Considerations ................................. 42

3.3 The Spectrometer .................................................... 45

3.3.1 The Vacuum System ........................................... 45

3.3.2 The Electron Energy Analyser ............................... 49

3.3.3 The Light Source Unit ......................................... 54

3.3.4 The Sample System ............................................. 57

(a) General Sample Inlet System ................................. 57

(b) Direct Inlets for Reactive Molecules ......................... 57

(c) Microwave Discharge Unit for Producing Transients ....... 58

(d) High Temperature Pyrolysis Unit for Producing Transients 61

(e) Variable Temperature Unit for Equilibrium Studies ....... 63

3.3.5 The Scanning and Detection System ......................... 65

3.4 Operation and Performance of the Spectrometer ............... 67

CHAPTER IV: PHOTOELECTRON SPECTROSCOPY OF SOME TRANSIENT SPECIES

4.1 Carbon Monosulfide (CS) ......................................... 76

4.1.1 Introduction .................................................... 76

4.1.2 Experimental ................................................... 77

4.1.3 Results and Discussion ....................................... 78

4.2 Sulfur Monoxide (SO) .............................................. 84
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2.1</td>
<td>Introduction</td>
<td>84</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Experimental</td>
<td>85</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Results and Discussion</td>
<td>85</td>
</tr>
<tr>
<td>4.3</td>
<td>Disulfur Monoxide ($S_2O$)</td>
<td>94</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Introduction</td>
<td>94</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Experimental</td>
<td>95</td>
</tr>
<tr>
<td>4.3.3</td>
<td>Results and Discussion</td>
<td>96</td>
</tr>
<tr>
<td>4.4</td>
<td>Diazenes (HN=NH) and Diazenes-d$_2$ (DN=ND)</td>
<td>104</td>
</tr>
<tr>
<td>4.4.1</td>
<td>Introduction</td>
<td>104</td>
</tr>
<tr>
<td>4.4.2</td>
<td>Experimental</td>
<td>105</td>
</tr>
<tr>
<td>4.4.3</td>
<td>Results</td>
<td>107</td>
</tr>
<tr>
<td>4.4.4</td>
<td>Discussion</td>
<td>118</td>
</tr>
<tr>
<td>4.5</td>
<td>Trans-methyldiazenes (CH$_3$N=NH)</td>
<td>123</td>
</tr>
<tr>
<td>5.1</td>
<td>Methyliophosphide (HCP)</td>
<td>128</td>
</tr>
<tr>
<td>5.1.1</td>
<td>Introduction</td>
<td>128</td>
</tr>
<tr>
<td>5.1.2</td>
<td>Experimental</td>
<td>128</td>
</tr>
<tr>
<td>5.1.3</td>
<td>Results and Discussion</td>
<td>130</td>
</tr>
<tr>
<td>5.2</td>
<td>CSe$_2$, OCSe and SCSe</td>
<td>133</td>
</tr>
<tr>
<td>5.2.1</td>
<td>Introduction</td>
<td>133</td>
</tr>
<tr>
<td>5.2.2</td>
<td>Experimental</td>
<td>135</td>
</tr>
<tr>
<td>5.2.3</td>
<td>Results</td>
<td>136</td>
</tr>
<tr>
<td>5.2.4</td>
<td>Discussion</td>
<td>147</td>
</tr>
<tr>
<td>5.3</td>
<td>Ozone (O$_3$)</td>
<td>163</td>
</tr>
</tbody>
</table>
5.3.1 Introduction ........................................ 163
5.3.2 Experimental ....................................... 163
5.3.3 Results and Discussion ............................. 164
5.4 Nitrosyl Halides (XNO, X = F, Cl, Br) ............. 174
   5.4.1 Introduction .................................... 174
   5.4.2 Experimental ................................... 175
   5.4.3 Results ........................................... 175
   5.4.4 Discussion ...................................... 179
5.5 Nitric Acid (HNO₃) and Nitryl Halides (XNO₂, X = F, Cl) ........................................ 184
   5.5.1 Introduction .................................... 184
   5.5.2 Experimental ................................... 185
   5.5.3 Results ........................................... 185
   5.5.4 Discussion ...................................... 193
CHAPTER VI: CONCLUSION .................................. 202
REFERENCES .................................................. 206
APPENDIX ..................................................... 221
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Correlation Between the Franck-Condon Principle and the Shape of PE Bands</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>for the Removal of Electrons from Molecular Orbitals of Different Bonding</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Character</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Doppler Broadening (a) As a Function of Electron Kinetic Energy ($E_{\text{kin}}$)</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>for Different Molecular Weights ($M$); (b) As a Function of Temperature</td>
<td></td>
</tr>
<tr>
<td></td>
<td>for Different $E_{\text{kin}}/M$ Values</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Plate of the Photoelectron Spectrometer</td>
<td>46</td>
</tr>
<tr>
<td>4.</td>
<td>Vertical Cross-Section of the Spectrometer Through the Entrance and Exit</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>Apertures of the Electron Energy Analyzer</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Plate of the Spectrometer Showing the General Sample Inlets, the Pumping</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>Ports for the Ionization Chamber, the Analyzer and the Electron Multiplier</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Schematic Diagram of 180° Hemispherical Electrostatic Analyzer Unit</td>
<td>51</td>
</tr>
<tr>
<td>7.</td>
<td>Vertical Cross-Section of the Light Source Unit</td>
<td>56</td>
</tr>
<tr>
<td>8.</td>
<td>Plate of the Kel-F and Pyrex Direct Sample Inlets</td>
<td>59</td>
</tr>
<tr>
<td>9.</td>
<td>Plate of the Microwave Discharge Assembly</td>
<td>60</td>
</tr>
<tr>
<td>10.</td>
<td>Plate of the High Temperature Pyrolysis Unit</td>
<td>62</td>
</tr>
<tr>
<td>11.</td>
<td>Plate of the Variable Temperature Unit</td>
<td>64</td>
</tr>
<tr>
<td>12.</td>
<td>Diagrams of the Control Circuitry</td>
<td>66</td>
</tr>
<tr>
<td>13.</td>
<td>PE Spectra of Oxygen Recorded by Different Scanning Modes</td>
<td>69</td>
</tr>
<tr>
<td>14.</td>
<td>PE Spectra of (a) Atomic Hydrogen and (b) Atomic Nitrogen and Vibrational</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>Excited Nitrogen</td>
<td></td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>15. PE Spectra of Atomic Fluorine</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>16. PE Spectrum of O$_2$(^1Δ$_g$) and Atomic Oxygen</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>17. PE Spectra of (a) CS$_2$ and (b) The Products of a MW Discharge in CS$_2$</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>18. The Individual PE Bands of CS</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>19. PE Spectra of SO in the Presence of SO$_2$ and S$_2$O</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>20. The First PE Band of SO at High Resolution</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>21. Parts of the PE Spectra of SO$_2$ (A) and the Products of a MW Discharge in SO$_2$ (B) at High Resolution</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>22. The Second, Third and Fourth PE Bands of SO at high Resolution</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>23. PE Spectra of (a) SO$_2$, (b) SOCl$_2$, After Being Passed Over Hot Ag$_2$S and (c) SOCl$_2$</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>24. Correlation Diagram for the IP's of SO$_2$, S$_2$O, NSCl and NSF</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>25. The First, Second and Third PE Bands of S$_2$O</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>26. PE Spectra of (a) N$_2$H$_2$, (b) Volatile Products of a MW Discharge in N$_2$H$_4$, (c), (d) and (e) Mixture (b) After Addition of Increasing Amount of HCl</td>
<td>108</td>
<td></td>
</tr>
<tr>
<td>27. PE Spectra of (a) N$_2$D$_4$ and (b) The Products of a MW Discharge in N$_2$D$_4$</td>
<td>109</td>
<td></td>
</tr>
<tr>
<td>28. PE Spectra of the First Bands of N$_2$D$_2$ and ND$_3$ After Addition of Increasing Amount of DCl</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>29. NH$_3$-Free PE Spectrum of N$_2$H$_2$</td>
<td>113</td>
<td></td>
</tr>
<tr>
<td>30. The Individual PE Bands of N$_2$H$_2$</td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>31. The Individual PE Bands of N$_2$D$_2$</td>
<td>117</td>
<td></td>
</tr>
<tr>
<td>32. PE Spectra of (a) CH$_3$N=NH and (b) CH$_3$N=NCH$_3$</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>33. Carbon Arc Reactor for the Synthesis of HCP</td>
<td>129</td>
<td></td>
</tr>
<tr>
<td>34. PE Spectrum of HCP in the Presence of C$_2$H$_2$</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>35. PE Spectra of (a) CO₂, (b) CS₂, (c) CSe₂, (d) OCS, (e) OCSe and (f) SCSe</td>
<td>137</td>
<td></td>
</tr>
<tr>
<td>36. The Second and Third PE Bands of CSe₂</td>
<td>142</td>
<td></td>
</tr>
<tr>
<td>37. The Individual PE Bands of OCSe; (a) First, Second, (c) Third and (d) Fourth Bands</td>
<td>144</td>
<td></td>
</tr>
<tr>
<td>38. The Individual PE Bands of SCSe; (a) First, (b) Second, (c) Third and (d) Fourth Bands</td>
<td>146</td>
<td></td>
</tr>
<tr>
<td>39. Correlation Diagram for the IP's of CO₂, CS₂, CSe₂, OCS, OCSe and SCSe</td>
<td>149</td>
<td></td>
</tr>
<tr>
<td>40. HeI PE Spectrum of O₃</td>
<td>165</td>
<td></td>
</tr>
<tr>
<td>41. The First, Second and Third PE Bands of O₃ using (a) HeI and (b) NeI Light Sources</td>
<td>166</td>
<td></td>
</tr>
<tr>
<td>42. PE Spectra of (a) FNO, (b) ClNO and (c) BrNO</td>
<td>176</td>
<td></td>
</tr>
<tr>
<td>43. PE Spectra of (a) HNO₃, (b) ClNO₂ and (c) FNO₂</td>
<td>186</td>
<td></td>
</tr>
<tr>
<td>44. The Lower Energy PE Bands of (a) HNO₃, (b) ClNO₂ and (c) FNO₂ at High Resolution</td>
<td>194</td>
<td></td>
</tr>
<tr>
<td>45. Correlation Diagram for the IP's of NO₂, CH₃NO₂, HNO₃, ClNO₂ and FNO₂</td>
<td>200</td>
<td></td>
</tr>
</tbody>
</table>
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Monochromatic Photon Sources for Use in Photo-electron Spectroscopy</td>
<td>2</td>
</tr>
<tr>
<td>2. Experimental Half-Width and Intensity of the Argon $^2P_{3/2}$ Peak at Different Focusing Conditions of the Analyzer</td>
<td>71</td>
</tr>
<tr>
<td>3. PES and Theoretical Data for CS</td>
<td>80</td>
</tr>
<tr>
<td>4. PES Data for SO</td>
<td>89</td>
</tr>
<tr>
<td>5. PES and Theoretical Data for $S_2O$</td>
<td>98</td>
</tr>
<tr>
<td>6. PES Data for $N_2H_2$ and $N_2D_2$</td>
<td>112</td>
</tr>
<tr>
<td>7. PES and Theoretical Data for $CH_3N=NH$</td>
<td>127</td>
</tr>
<tr>
<td>8. PES and Theoretical Data for HCP</td>
<td>132</td>
</tr>
<tr>
<td>9. PES Data for $CO_2$, $CS_2$, $CSe_2$, OCS, OCS, and SCSe.</td>
<td>138</td>
</tr>
<tr>
<td>10. (a) Experimental and Calculated Franck-Condon Factors in the Individual States of $CO_2^+$, $CS_2^+$ and $CSe_2^+$</td>
<td>152</td>
</tr>
<tr>
<td>(b) Experimental and Calculated Franck-Condon Factors in the Individual States of $OCS^+$, $OCSe^+$ and $SCSe^+$</td>
<td>154</td>
</tr>
<tr>
<td>11. Estimated Bond Lengths of the Individual States of $CO_2^+$, $CS_2^+$, $CSe_2^+$, $OCS^+$, $OCSe^+$, $SCSe^+$ and $N_2O^+$</td>
<td>159</td>
</tr>
<tr>
<td>12. PES and Theoretical Data for $O_3$</td>
<td>169</td>
</tr>
<tr>
<td>13. PES Data for the Nitrosyl Halides (XNO)</td>
<td>177</td>
</tr>
<tr>
<td>14. SCF-MO Results for the Nitrosyl Halides</td>
<td>180</td>
</tr>
<tr>
<td>15. PES and Theoretical Data for $HNO_3$, $ClNO_2$ and $FNO_2$</td>
<td>188</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

I would like to express my sincere appreciation and gratitude to Dr. D. C. Frost and Dr. C. A. McDowell for their continued support, understanding and guidance throughout the course of this work.

I would also like to thank my many colleagues, Mr. A. Bain, Dr. J. C. Bunzli, Dr. M. Chiang, Mr. T. Chau, Dr. L. S. Chia, Dr. A. B. Cornford, Dr. A. Katrib, Dr. D. J. Smith, Dr. N. P. C. Westwood, Dr. G. Wight and Mr. D. Yee for their assistance on many occasions. Thanks are also due to Dr. R. Boyd, Dr. C. E. Brion, Dr. F. G. Herring, Dr. H. Kroto, Dr. A. J. Merer and Dr. R. Tapping for helpful discussions.

I wish to acknowledge gratefully the staff of the Electronic, Glass, Illustration and Mechanical Workshops. I am specially grateful to Mr. E. Matter for his precision construction of the spectrometer and to Mr. C. McCafferty for his skillful technical assistance.

I am thankful to Dr. N. P. C. Westwood for a careful
reading of this manuscript, to Mr. Paul Tang for typing part of the first draft and to Miss Patti Hon for typing the thesis.

I wish to extend my appreciation to all our friends who made our residence in Vancouver most enjoyable.

I am most grateful to my wife for her love, understanding and encouragement. I am indebted to my father for undergoing a lot of hardship in bringing me up. Our son Stanley should also be thanked for behaving himself during the writing of this thesis.
CHAPTER ONE

INTRODUCTION

Photoelectron spectroscopy is, essentially, a technique for measuring the binding energies or ionization potentials of electrons in molecules or atoms, by exposing the sample to a source of monochromatic photons of known energy $h\nu$ and analyzing the kinetic energies of the photoejected electrons. The binding energies $E_b$ of the different groups of electrons can be obtained from the measured kinetic energies $E_{kin}$ utilizing the Einstein photoelectric equation,

$$E_b = h\nu - E_{kin}. \quad (1)$$

The essential requirements for a photon source which is to be used in photoelectron spectroscopy are that it be monochromatic, of usable intensity, and have sufficient energy to ionize the electrons of interest. A list of such photon sources, together with their characteristics is shown in Table I. Depending upon the energy of the photon source, the overall
### TABLE 1. Monochromatic Photon Sources For Use in Photoelectron Spectroscopy

<table>
<thead>
<tr>
<th>X-Ray Photon Source</th>
<th>Energy (eV)</th>
<th>Wave Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag K(_\alpha)</td>
<td>22162.9</td>
<td>0.55941</td>
</tr>
<tr>
<td>Mo K(_\alpha)</td>
<td>17479.3</td>
<td>0.70930</td>
</tr>
<tr>
<td>Cu K(_\alpha)</td>
<td>8048</td>
<td>1.5405</td>
</tr>
<tr>
<td>Cr K(_\alpha)</td>
<td>5415</td>
<td>2.2896</td>
</tr>
<tr>
<td>Al K(_\alpha)</td>
<td>1486.6</td>
<td>8.399</td>
</tr>
<tr>
<td>Mg K(_\alpha)</td>
<td>1253.6</td>
<td>10.034</td>
</tr>
<tr>
<td>Na K(_\alpha)</td>
<td>1041.0</td>
<td>11.910</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>VUV Photon Source</th>
<th>Energy (eV)</th>
<th>Wave Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HeII</td>
<td>40.3126</td>
<td>303.731</td>
</tr>
<tr>
<td>HeI</td>
<td>21.2175</td>
<td>584.334</td>
</tr>
<tr>
<td>HeI doublet</td>
<td>16.8477/16.6704</td>
<td>735.895/743.718</td>
</tr>
<tr>
<td>ArI doublet</td>
<td>11.8273/11.6233</td>
<td>1048.219/10066.659</td>
</tr>
<tr>
<td>KrI doublet</td>
<td>10.6434/10.0321</td>
<td>1164.867/1235.838</td>
</tr>
<tr>
<td>H Lyman (\alpha)</td>
<td>10.1986</td>
<td>1215.668</td>
</tr>
<tr>
<td>XeI doublet</td>
<td>9.5697/8.4363</td>
<td>1295.586/1469.610</td>
</tr>
</tbody>
</table>

* indicates the more intense line of the doublet.
field of photoelectron spectroscopy falls into two branches. One branch uses higher energy X-ray sources, and is termed Electron Spectroscopy for Chemical Analysis (ESCA)\textsuperscript{1,2} or X-ray Photoelectron Spectroscopy (XPS). The other uses vacuum ultraviolet (VUV) radiation, and is called Molecular Photoelectron Spectroscopy\textsuperscript{3}, UV Photoelectron Spectroscopy (UPS), or simply Photoelectron Spectroscopy (PES). In ESCA, Aluminum K\textsubscript{\alpha} (1486.6 eV) and Magnesium K\textsubscript{\alpha} (1253.6 eV) are by far the most commonly used sources due to their narrower line widths, higher intensity and ease of operation, while the HeI resonance line (21.2175 eV) is most popularly used in PES for the same reasons. ESCA, because of its more energetic source and lower limiting resolution (>0.2 eV), is mainly concerned with the study of inner or core shell electrons. PES is exclusively concerned with outer or valence shell (up to about 40 eV) electrons. This leaves a gap between 40 eV and 1,000 eV where suitable photon sources are lacking, although recent developments indicate that this gap may be filled by the use of synchrotron radiation in conjunction with a monochromator\textsuperscript{4-6}. Yttrium X-ray lines at about 130 eV developed by Krause\textsuperscript{7} are also a promising source, although satellite lines are a complicating factor here. This thesis is concerned with PES using mainly the HeI resonance line.

In view of the fact that the basic principles of PES were well understood as early as 1905, when Einstein\textsuperscript{8} successfully explained the photoelectric effect, it is surprising that the first set of such experiments appeared only as late as the
early 1960's. Since then there has been an exponential growth in the field of PES as evidenced by the appearance of numerous extensive reviews, and the gathering of several international conferences. Within the past ten years or so, PES has developed from its exploratory stage to become one of the standard techniques of modern chemistry. Although the field is a young and developing one, it is generally acknowledged that it has at least reached its first stage of maturity. The primary goal of PES, which is to obtain molecular ionization potentials with high precision and resolution, has certainly been met judging from the fact that hundreds of spectra have been recorded and discussed in books and in the literature. Alerted by its potential, and with the availability of commercial photoelectron spectrometers, more and more researchers have begun to apply PES as a routine tool in molecular spectroscopy. In this respect, PES is essentially like any of the standard spectroscopic techniques, such as nmr, mass spectrometry, etc. To date, most of published PES work has been concerned with compounds that are stable under normal conditions, and have appreciable volatility (> 0.01 Torr) below 200°C. This kind of PES work will be called 'conventional' photoelectron spectroscopic studies in this thesis. On the other hand, PES studies of transient species and reactive molecules are rare because of the experimental difficulties involved. During the initial stages of this study, a few exploratory attempts to study such systems with the technique of PES had revealed its great potential in providing information on the chemical
bonding of transient species, which would normally be very difficult to obtain by other methods. The extension of PES to study reactive molecules, which can be handled and studied only under appropriately controlled conditions, would be very fruitful since these molecules play a significant role in chemistry.

This thesis will describe an attempt to extend PES into the realms of these 'unconventional' photoelectron spectroscopic studies. A photoelectron spectrometer suitable for this kind of work has been designed and constructed. With this spectrometer, some transient species and reactive molecules have been studied. In addition, it has been possible to vary the temperature of the sample between -180°C and +1,200°C, where temperature dependent equilibrium systems may be studied.
CHAPTER TWO

THEORY OF PHOTOELECTRON SPECTROSCOPY

Although photoelectron spectroscopy (PES) is a relatively new technique, its theory is well documented and has been discussed in great detail in numerous reviews \(^1-3, 13-37\). Therefore, except for those aspects which are more pertinent to the study in this thesis, only a brief summary of the basic principles of the theory will be presented here. Greater attention will be paid to those areas where new developments have been achieved.

2.1 Characteristics Of A Photoelectron Spectrum

When a photoelectron is ejected by a photon of energy \(h\nu\) from a molecule or atom, by the conservation of energy the following energy relation holds.

\[
h\nu = E_{\text{kin}} + E_r + I_0 + \Delta E_{\text{vib}} + \Delta E_{\text{rot}} + \Delta E_{\text{tran}}, \quad (2.1.1)
\]
where $E_{\text{kin}}$ is the kinetic energy of the photoelectron,

$E_r$ is the recoil energy of the ion,

$I_0$ is the difference in the electronic energy of the ion and molecule, and is termed the adiabatic ionization potential,

and $\Delta E_{\text{vib}}$, $\Delta E_{\text{rot}}$ and $\Delta E_{\text{tran}}$ are respectively the difference in the vibrational, rotational and translational energy of the ion and the parent molecule.

Because of the large difference in the mass of the ion and the ejected electron, $E_r$ is neglected through consideration of the conservation of momentum. Under the present level of experimental resolution ($>10 \text{ meV}$, see section 2.3), rotational and translational energy level are usually not resolved, and thus $\Delta E_{\text{rot}}$ and $\Delta E_{\text{tran}}$ are also neglected. Usually the molecule is in the ground vibrational state, thus eq. (2.1.1) reduces to

$$h\nu = E_{\text{kin}} + I_0 + E_{\text{vib}}^+$$

(2.1.2)

where $E_{\text{vib}}^+$ is the vibrational energy of the ion. The measurement of the kinetic energy of the electron then gives the ionization potential of the molecule.

The photoelectron (PE) spectrum of a molecule thus consists of several PE bands, each of which corresponds to an ionization potential (IP) of the molecule, all the way up to the energy of the incident photons. The integrated area or the intensity of the individual band is related to the differential photoionization cross section corresponding to that
ionic state, and the shape of the band is an indication of the geometry change upon ionization. Each or some of these bands may show a series of resolved peaks corresponding to the different vibronic states. The separations between these peaks are then the vibrational frequencies of the ion. The lowest energy (first) peak, or the onset of the PE band is normally the adiabatic IP, while the most intense peak or the maximum of the band is referred to as the vertical IP. If the molecule is vibrationally excited or there is a large change in geometry during ionization, then care should be exercised in locating the exact position of the adiabatic IP. The intensity of each individual peak in a PE band is proportional to the probability of producing that particular vibronic state, giving the so-called Franck-Condon Factor.

In addition to the above-mentioned vibrational fine structure, further band structure may be due to spin-orbit coupling, Jahn-Teller distortion, or a mixture of the two, i.e. the spin-vibronic interactions. For quasi-linear ionic states the possibility of the Renner-Teller effect exists. Complications to simple band shapes may arise through auto-ionization or predissociation, and must be considered in a rigorous analysis. For molecules having IP's less than \(1\) eV, additional bands corresponding to low energy photoelectrons may arise due to the impurity lines in the light source (see section 3.3.3).
2.2 The Interpretation Of Molecular PE Spectra

2.2.1 A Brief Survey Of Assignment Criteria

Assuming an orbital description of a molecule, then at a certain level of approximation the molecular PE spectrum is a direct display of the energies of the various molecular orbitals (MO's). The individual PE bands then correspond to the removal of an electron from each MO leaving the ion in different ionic states. The lowest energy band is usually associated with the ground ionic state, while the others correspond to excited ionic states. In this way, the PE spectrum of a molecule is similar to the electronic spectrum of the ion with the transitions occurring only between its occupied MO's. The quantitative correspondence between the energies of the bands or IP's and that of the orbitals from which the electrons are removed is expressed in Koopmans' theorem \(^{49}\) (see section 2.2.2) which states that the \(n^{th}\) IP can be approximated to the negative of the \(n^{th}\) orbital energy. With this theorem, the comparison of the calculated orbital energies and the experimental IP's is widely used in the interpretation of PE spectra.

The vibrational fine structures and the shapes of the individual PE bands frequently contain a great deal of information on the bonding characteristics of the orbital to which they relate. The relation between the band structures and orbital characteristics are derived from the Franck-Condon principle \(^{50,51}\), which will be discussed in section 2.2.3. A further indication of the bonding character of the orbital may
be obtained from the change of the vibrational frequencies on going from the molecule to the ion. This makes use of the close relationship between the vibrational frequency, the force constant and the bond order. Thus, if a nonbonding electron is removed, there will be practically no change in vibrational frequency, whereas if a bonding or antibonding electron is removed, the vibrational frequency of the ion will be less or greater respectively than that of the neutral molecule. In larger polyatomics, several vibrational modes may be excited upon ionization, thus making vibrational assignments more difficult. Occasionally, the analysis of the spin orbit,\textsuperscript{52,53} Jahn-Teller\textsuperscript{54-57} and Renner-Teller\textsuperscript{58,59} splittings can be fruitful and lead to a better understanding of the structure of the ion.

A useful approach, especially for complex molecules, is to study a large number of homologous compounds\textsuperscript{60,61}. By studying many such related compounds, and correlating and comparing the spectra down a series, one can usually gain some information that would not be obvious otherwise. In such studies, one may also make use of the resonance and inductive effects of the substituent groups. For planar molecules where applicable, the perfluoro effect\textsuperscript{62,63} may sometimes be used to differentiate the $\pi$ and $\sigma$ orbitals.

Sometimes, the relative intensities of the bands may be used as an indication of the degeneracy of the states, i.e. the degenerate states have greater intensities than the non-degenerate states. This guideline must be used with
caution since it has been found invalid in many cases.\textsuperscript{17} Quite recently the study of photoionization cross sections as a function of ionizing energy has shown high potential in providing information on the bonding character of orbitals. Both experimental\textsuperscript{64,65} and theoretical\textsuperscript{66} studies have indicated that usually the intensities of the orbitals mainly of s character tend to increase with respect to that of the orbitals mainly of p character when using higher energy light sources. The theoretical studies\textsuperscript{66-69} have indicated some interesting relationships between the energy dependence of photoionization cross sections and the bonding character of orbitals. In view of the success of these studies, the comparison of measured and calculated values for relative band intensities may become an additional useful assignment criterion in PES. Another related and promising technique is the study of the intensity of the ejected photoelectrons as a function of the angle between the direction of the incoming photon and the outgoing photoelectron. This may also shed light on the nature of the molecular orbital, through the determination of the $B$ factor.\textsuperscript{70,71} PES is not a threshold technique, consequently the spectra are generally not complicated by autoionization processes. On the contrary, because of its resonant nature, autoionization in PES can usually be identified by using different light sources, and often leads to useful information about the autoionized state.
2.2.2 Koopmans' Theorem And The Calculation of Vertical IP's

(a) Koopmans' Theorem and Its Implications

Consider a two-step process:

(1) Calculation of a Hartree-Fock (HF) Self-Consistent-Field (SCF) wave function for a molecule with \( n \) doubly occupied molecular orbitals and evaluation of its total energy \( E \).

(2) Evaluation of the single determinant energy of the ion \( E^+ \) resulting from the removal of an electron from the \( k^{\text{th}} \) molecular orbital, using the HF-SCF orbitals from the above calculation of the molecule for the remaining electrons.

Koopmans showed that the energy difference or IP calculated in this way is just the negative of the \( k^{\text{th}} \) orbital energy.

The mathematical proof of Koopmans' theorem (KT) is quite straightforward. For a molecule with \( n \) doubly occupied MO's \( \phi_i \), the single determinant wavefunction is

\[
\psi = |\phi_1(1)\phi_1(2)\cdots\phi_k(2k-1)\phi_k(2k)\cdots\phi_n(2n-1)\phi_n(2n)|, \quad (2.2.1)
\]

and the Hamiltonian of the molecule is

\[
H = \sum_{i=1}^{2n} \left( -\frac{\nabla_i^2}{2} - \sum_{\alpha=1}^{K} \frac{Z_{\alpha}}{R_{\alpha i}} \right) + \sum_{i<j}^{2n} \frac{1}{r_{ij}}. \quad (2.2.2)
\]

The corresponding wavefunction and the Hamiltonian for the ion with an electron removed from the \( k^{\text{th}} \) MO are
\[ \psi^+ = |\phi_1(1)\phi_2(2)\cdots \{\phi_k(2k-1)\} \cdots \phi_n(2n-1)\phi_n(2n)| \]

(2.2.3)

and

\[ H^+ = \sum_{i=1}^{2n-1} \left( \frac{v_i^2}{2} - \sum_{\alpha=1}^{K} \frac{Z_\alpha}{R_{\alpha i}} \right) + \sum_{i<j}^{2n-1} \frac{1}{r_{ij}} . \]  

(2.2.4)

In the expression for the Hamiltonians, \( Z_\alpha \) is the charge on the nucleus \( \alpha \), \( r_{\alpha i} \) is the distance of the electron \( i \) from the nucleus \( \alpha \), and \( r_{ij} \) is the distance between electron \( i \) and \( j \). It can be shown\(^{74}\) that the total energy of the molecule and the ion are

\[ E = 2 \sum_{i=1}^{n} h_i + \sum_{i,j=1}^{n} (2J_{ij} - K_{ij}) \]  

(2.2.5)

and

\[ E^+ = 2 \sum_{i=1}^{n} h_i + \sum_{i,j=1}^{n} (2J_{ij} - K_{ij}) + h_k \]

\[ + \sum_{i=1}^{n} (2J_{ik} - K_{ik}) \]  

(2.2.6)

where

\[ h_i = \int_{\phi_i^+(1)} \left( -\frac{v_i^2}{2} - \sum_{\alpha=1}^{K} \frac{Z_\alpha}{R_{\alpha i}} \right) \phi_i(1) dr_1 \]  

(2.2.7)
= energy of an electron alone in the field of the bare nuclei; comprising the kinetic and electron-nuclear attraction energy,

\[ J_{ij} = \int \int \phi_i^*(1) \phi_j^*(2) \frac{1}{r_{12}} \phi_i(1) \phi_j(2) dr_1 dr_2 \quad (2.2.8) \]

= coulombic repulsion between any electron pair,

and

\[ K_{ij} = \int \int \phi_i^*(1) \phi_j^*(2) \frac{1}{r_{12}} \phi_i(2) \phi_j(1) dr_1 dr_2 \quad (2.2.9) \]

= exchange interaction between any electron pair of the same spin.

Noting \( J_{ii} = K_{ii} \), one obtains

\[ E^+ - E = -h_k - \sum_{i=1}^{n} (2J_{ik} - K_{ik}) . \quad (2.2.10) \]

Since, however, the \( k^{th} \) orbital energy \( \epsilon_k \) is given by the solution of the SCF equation, i.e.

\[ \left( -\frac{\hbar^2}{2m} - \sum_{\alpha=1}^{K} \frac{Z_{\alpha}}{R_{\alpha}} \right) + \sum_{i=1}^{n} (2J_i - K_i) \phi_k = \epsilon_k \phi_k , \quad (2.2.11) \]

then one has
\[ \varepsilon_k = \hbar_k + \sum_{i=1}^{n} (2J_{ik} - K_{ik}), \quad (2.2.12) \]

and hence

\[ E^+ - E = -\varepsilon_k. \quad (2.2.13) \]

This thus illustrates the validity of KT.

There are three kinds of errors in the IP's calculated by this method due to:

1. The relaxation of the orbitals in the ion due to the perturbation caused by ionization.
2. The difference in electron correlation energy in the ion and the molecule.
3. The difference in relativistic energy in the ion and the molecule.

The neglect of (1) is inherent in KT and results in the calculated IP's being too large. Because of this neglect, the calculated IP should correspond to the vertical IP. (2) and (3) are introduced in the HF-SCF-MO method which is used to calculate the molecular wave function and the orbital energies. This method makes no attempt to calculate relativistic energy in both the ion and the molecule, with the IP being given only by the difference in electrostatic energy. Since the relativistic effect increases with the kinetic energy of the electron, the correction for this effect is usually negligible for outer shell electrons but is appreciable for
inner shell electrons. The HF theory includes some electron correlation by assuming that electron experiences an average potential created by the remaining \((2n-1)\) electrons and through imposing the Pauli exclusion principle on the wave function. As such, the HF theory neglects the instantaneous (rather than average) repulsions between pairs of electrons. The contribution to the total energy due to instantaneous repulsions is called the correlation energy\(^{73}\), since the motion of the electrons is correlated such that two electrons are unlikely to get very close to each other due to the coulombic repulsion. While the Pauli principle ensures the avoidance of electrons with parallel spins, in the independent-particle (one orbital per electron) HF scheme, the major part of the correlation error comes from the neglect of spatial correlation between the electrons with antiparallel spins. Since correlation effects arise to a large extent from pair interactions between electrons, the correlation energy is usually less in the ion than the molecule. As a result, generally too small an IP will be given by the difference of the good HF energies of the ion and molecule calculated independently.

(b) Application of Koopmans' Theorem in PES

Fortunately the errors introduced by the neglect of the relaxation and correlation effects are of opposite sign and very often tend to cancel each other. Therefore, IP's calculated by assuming KT frequently predict the experimental
values within a reasonable degree of accuracy. It has been shown\textsuperscript{74,75} that the application of KT to calculations near HF accuracy of outer shell orbital energies often gives IP's too high by \( \approx 8\% \). This tends to indicate that, in general, the error due to relaxation energy is larger than the correlation energy. The \( \approx 92\% \) agreement between experimental and calculated IP's is often sufficient to assign the photoelectron spectra unambiguously. Because of its simplicity and economy, KT IP's calculated by semi-empirical SCF-MO schemes such as the CNDO\textsuperscript{76}, INDO\textsuperscript{76}, MINDO\textsuperscript{77} and extended Hückel\textsuperscript{78} methods are more widely used than ab initio calculations. In addition to the assumptions of KT, the success of these methods depends on its inherent approximations. Very often, the relative ordering of the orbitals derived from the semi-empirical methods are the same as the ab initio result, although the orbital energies may be quite different. In such cases, the assignment of the PE spectrum would be the same. Experience\textsuperscript{79} has shown the IP's calculated by CNDO/2\textsuperscript{76} and INDO\textsuperscript{76} methods are generally \( \approx 4 \) eV larger than the experimental values.

Despite the general success of KT for closed-shell molecules, its breakdown in predicting the right ordering of the ionic states is not uncommon. The classical case is \( \text{N}_2 \text{O}_2 \textsuperscript{80} \), where KT predicts \( 2\pi_u \) rather than \( 2\pi_g^+ \) being the ground ionic state. Other notable examples are in \( \text{F}_2 \textsuperscript{31}, \text{CO}_2 \textsuperscript{3}, \text{CS}_2 \textsuperscript{3}, \) and OCS\textsuperscript{3}. An extreme case is provided by bis(\( \pi \)-allyl)nickel,
whose first IP at 7.85 eV\textsuperscript{82} corresponds to the almost pure Ni-3d orbital\textsuperscript{83} (9a\textsubscript{g}) of the neutral molecules. This, in fact, is the 13\textsuperscript{th} orbital counted from the highest occupied orbital (7a\textsubscript{u}). Ab initio calculations\textsuperscript{44} showed that $\epsilon(9a\textsubscript{g}) = -18.3$ eV, whereas separate calculations\textsuperscript{84} of the ion and molecule gave the same IP at 7.92 eV after relaxation of the electrons. This value is then in good agreement with experiment. Some guidelines in the safe use of KT and in forecasting the situations where KT is mostly likely to fail have been given in the literature\textsuperscript{85-88}. In general, KT is mostly likely to fail when the ionization perturbation gives rise to large orbital reorganization. In particular, this includes the cases when the electron being removed is localized in one part of the molecule\textsuperscript{88}, either due to symmetry reasons or because it is a 'lone pair' electron. For the same reason, molecules containing electron-rich atoms like F tend to deviate from KT. Particular care must be exercised in the case where two or more orbitals lie close together, and where more often than not the relative ordering is problematical, leading to doubts in assigning the experimental IP's.

(c) Other Methods For Calculating Vertical IP's

It is obvious that the correct way of getting accurate IP's is to perform independent calculations for the molecule and the individual state of the ion, including the correlation energy and, perhaps, relativistic energy. Except for simple
molecules, this process is tedious and expensive, if feasible, and is not expected to be popular in the near future. Partly because of this, considerable effort has been recently attempted to correct the inefficiency of KT. One approach has invoked the many-body techniques of second quantization, by which the vertical IP is directly related to the poles of the one particle Green's function. Application of this method to \( N_2 \) and \( F_2 \) showed very good agreement with experiment. This method appears to be very promising in spite of its rather elaborate computations. Another approach used the Rayleigh-Schrödinger perturbation theory to correct the wavefunctions and energies of the ion and molecule. With first order corrections to the wavefunction, third order correction to the energy, and using a basis set of double or one and half zeta Slater orbitals for the calculation, this method was able to reproduce experimental IP's with an absolute deviation of less than 0.5 eV.

(d) Open Shell Molecules

For open shell molecules, there are two more difficulties in applying KT in addition to the three limitations mentioned in the case of closed shell molecules. First, if the restricted SCF formalism is used, the off-diagonal multipliers \( \epsilon_{ij} \)'s, which are introduced as the Lagrangian multipliers by the constraints of the orthogonality of orbitals, cannot always be eliminated as they are in the
closed shell counterparts. Under such circumstances, as a result, no physical meaning can be attached to the diagonal $\varepsilon_{ij}$'s, which can be interpreted as orbital energies when $\varepsilon_{ij}$'s have been diagonalized. Therefore, in essence, KT does not hold. Even if the $\varepsilon_{ij}$'s can be eliminated, KT applies only in a limited sense. Generally, it holds for the open shell orbitals and not for the closed shell orbitals in the same molecule. If the unrestricted SCF formalism$^{103,106}$ is used, then $\varepsilon_{ij}$'s can be diagonalized, and the physical interpretation of orbital energies is possible. However, due to the fact that orbitals of different spins are different and thus have different energies, the one-to-one correspondence between the orbital energies and the IP's is lost. Secondly, in order that they be the eigenfunctions of the spin operators $S^2$ and $S_z$, the wave functions of the open shell states may not be single Slater determinants. As a result, the energy expression for such states contains cross terms due to the matrix elements between the component determinants, and thus KT usually does not apply. In practice, the first difficulty is not as bad as it looks since the orbital energies calculated in both formalisms often show qualitative agreements with the experimental IP's. An approximate way of estimating IP's for closed shell orbitals is to calculate them as excitation energies from the ground ionic state using its wave function (frozen orbital approximation). This was in fact the case in the study of the radicals $\text{NF}_2$$^{107}$, $\text{ClO}_2$$^{108}$ and $\text{NO}_2$$^{109}$, with
limited success. Naturally, the proper way would again be to
carry out independent calculations for the molecule and the
individual ionic states. But then, besides being tedious and
expensive, the calculation may have the added problem of
convergence. This difficulty was exemplified in the study
of NO$_2$.

2.2.3 Franck-Condon Principle in PES

(a) Wave Mechanical Formulation of The Franck-Condon (FC)
Principle$^{50,51}$.

The probability of a transition between two states
is proportional to the square of the electric dipole transition
integral $R$ given by

$$R = \int \psi'(q,Q)(R_n + R_e)\psi''(q,Q)dqdQ . \quad (2.2.14)$$

In this integral $\psi'(q,Q)$ and $\psi''(q,Q)$ are the total wavefunctions
describing the upper and lower quantum states, respectively,
indicated as functions of the totality of electronic coordinates
$q$ and the totality of nuclear coordinates $Q$, and $R_n$ and $R_e$ are
the nuclear and electronic dipole moment operators respectively.
Using the Born-Oppenheimer approximation$^{110}$, the wavefunction
can be separated into a product of electronic and nuclear
functions giving
\[ \psi(q,Q) = \psi_e(q,Q) \psi_n(Q). \quad (2.2.15) \]

Separating the nuclear function into the vibrational and rotational parts, the expression then becomes

\[ \psi(q,Q) = \psi_e(q,Q) \psi_v(Q) \psi_{\text{rot}}(Q), \quad (2.2.16) \]

where interactions between electronic, vibrational and rotational motion have been neglected. The rotational wavefunction can be neglected, since the relative intensities of the various vibrational peaks are of interest here. Thus we have

\[ R = \int \psi_e^* (q,Q) \psi_v^* (Q) (R_n + R_e) \psi_e^* (q,Q) \psi_v^* (Q) dQ dQ, \]

\[ (2.2.17) \]

which upon expanding gives

\[ R = \int \psi_v^* (Q) R_n \psi_v^* (Q) dQ \psi_e^* (q,Q) \psi_e^* (q,Q) dq + \]
\[ \int \psi_v^* (Q) R_e \psi_e^* (q,Q) \psi_e^* (q,Q) dq. \]

\[ (2.2.18) \]

By the orthogonality of \( \psi_e^* \) and \( \psi_e^* \), the first term vanishes. Denoting the electronic integral (the electronic transition moment) in the second term
\[ R_e(Q) = \int \psi_e^*(q,Q) R_e \psi_e^*(q,Q) dq, \quad (2.2.19) \]

and expanding it in a Taylor series about the equilibrium nuclear position \( Q_0 \) gives

\[ R_e(Q) = R_e(Q_0) + \left( \frac{dR_e}{dQ} \right)_{Q_0} (Q-Q_0) + \ldots. \quad (2.2.20) \]

The FC principle is based on the assumption\(^5\) that the variation of \( R_e \) with \( Q \) is slow, and thus all except the first term can be dropped, giving

\[ R = R_e(Q_0) \int \psi_v^* \psi_v^" dQ. \quad (2.2.21) \]

The vibrational transition probability or intensity is then

\[ I_{\psi_v^*, \psi_v^"} = \left| \int \psi_v^* \psi_v^" dQ \right|^2. \quad (2.2.22) \]

Equation (2.2.22) embodies the wave mechanical description of the FC principle: The intensity of a vibrational peak in an electronically allowed transition is proportional to the absolute square of the overlap integral, i.e. the FC factor, of the corresponding vibrational wavefunctions of the initial and final states. The FC factor is, in general, appreciable only when the maxima or minima of the two wavefunctions lie on top
of each other, i.e. at the same $Q$, and these maxima or minima for the higher vibrational levels appear near classical turning points of the motion, and thus vertical electronic transitions are usually the most favorable. This is in agreement with the result of the primitive form\textsuperscript{50} of the FC principle, stating that the electronic transition is so rapid with respect to the vibrational motion that the molecule maintains a fixed geometry immediately after the transition.

(b) Qualitative Application Of The FC Principle In PES

The influence of this principle on the vibrational patterns and band shapes observed in the PE spectrum of a diatomic molecule is illustrated in Fig. 1. The shaded area, frequently called the FC region, represents the vertical transitions allowed by the FC principle. The different band structures are determined by the potential curve of the resulting ion, which is in turn determined by the equilibrium internuclear distance and vibrational frequency of the ion. Depending upon whether the ejected photoelectron came from a bonding, antibonding or nonbonding orbital, the equilibrium internuclear distance in the ion may be greater, smaller or approximately the same as that in the parent molecule, while the opposite is true for the vibrational frequency due to the corresponding change in force constant. These changes in geometry and vibrational frequency will then determine, through the FC principle (see also the following section), where the
FIGURE 1

1. Nonbonding
2. Anti-bonding
3. Bonding
4. Strong Bonding
5. Dissociation
6. Curve Crossing
7. Predissociation by

IONIZATION POTENTIAL (eV)

INTERNUCLEAR DISTANCE, r
ion will be formed on the potential curve, giving rise to the various PE band structures as depicted in Fig. 1. Thus from the PE band shape and the vibrational frequency, the bonding character of the corresponding orbital from which the photoelectron is removed can frequently be deduced.

In the case of polyatomic molecules, the correlation between band shapes, vibrational frequencies, and bonding character becomes somewhat more complicated since the transitions now take place between multidimensional potential surfaces, and changes in bond lengths and bond angles are possible. Several vibrational modes may therefore be excited simultaneously. In addition, the bonding character of the MO's are now only meaningful between neighboring atom pairs in a molecule. Indeed, the same orbital can have different bonding character between different atom pairs, which means that, within the same band, one particular vibrational frequency may increase and another decrease, and the band structures of different vibrational progressions may be different. In general, however, the same principle applicable to the diatomic case may be used as a useful guide to the orbital nature in polyatomics.

(c) Quantitative Application Of The FC Principle In PES

According to the equation (2.2.22), the relative vibrational transition probabilities or intensities within a PE band are proportional to the corresponding FC factors.
These FC factors can be evaluated provided the appropriate vibrational wavefunctions are available. By calculating and fitting FC factors to the experimentally determined values, the geometry of the upper state can be estimated. This principle has, in fact, been frequently used to determine the geometries of excited electronic states observed in electronic spectra$^{112-115}$. The same concept$^{116}$ is also applicable in PES for estimating the geometry of the ionic states. This is particularly attractive since the structures of ions are normally difficult to obtain, especially for polyatomics.

The main task in such a quantitative investigation is the evaluation of the overlap integral

$$ M = \int \psi'(Q') \psi''(Q'') dQ', $$

(2.2.23)

where $Q'$ and $Q''$ denote the totality of normal coordinates in the ionic and molecular states respectively. Assuming that the vibrational wavefunction of each state has the form

$$ \psi_v = \prod_{i=1}^{n} \phi_i(Q_i), $$

(2.2.24)

then the overlap integral becomes

$$ M = \int \left[ \prod_{i=1}^{n} \phi'(Q'_i) \right] \left[ \prod_{i=1}^{n} \phi''(Q''_i) \right] dQ'_1 dQ'_2 \ldots dQ'_n. $$

(2.2.25)
In order to evaluate this integral it is necessary to specify the transformation between $Q'_j$'s and $Q''_i$'s, which are related by

$$Q' = AQ'' + d$$  \hspace{1cm} (2.2.26)

where $A$ is an $n \times n$ square matrix and $d$ is a column vector of order $n$. Normally $A_{ij}$ is different from zero only when the $i^{th}$ and $j^{th}$ normal coordinates have the same symmetry. For non-totally symmetric $Q'_i$, $d_i$ must be zero by symmetry.

Since $\psi''$ is usually a vibrationless ground state and is largely concentrated around the origin of the normal coordinates, the overlap integral is dominated by the contribution in the region of $Q'' = 0$ and $Q' = d$. In this case the integral will be insensitive to the nature of $A$, since the wavefunctions are the products of exponential terms. The integral may then be approximated by choosing $A$ to be a unit matrix, giving

$$Q'_i = Q''_i + d_i.$$  \hspace{1cm} (2.2.27)

Consequently, $M$ separates into $n$ component overlap integrals

$$M = \prod_{i=1}^{n} M_i(v'_i, v''_j),$$  \hspace{1cm} (2.2.28)
where

\[ M_i(v_i^1, v_j^1) = \int_{v_i} \phi_i^1 (Q_i^1) \phi_j^1 (Q_j^1 - d_i)dQ_i^1 \]  \hspace{1cm} (2.2.29)

The observed FC factors in the PE band may then be analyzed in terms of the squares of these one-dimensional integrals to give \( d_i \)'s.

For symmetry coordinates, we have\(^{118}\)

\[ S' = S'' + D \]  \hspace{1cm} (2.2.30)

and if

\[ S' = L'Q'; \quad S'' = L''Q'' \]  \hspace{1cm} (2.2.31)

then

\[ Q' = (L')^{-1}L''Q'' + (L')^{-1}D \]  \hspace{1cm} (2.2.32)

hence

\[ A = (L')^{-1}L'' \]  \hspace{1cm} (2.2.33)

\[ d = (L')^{-1}D \text{ or } D = L'd \]  \hspace{1cm} (2.2.34)

Therefore, a knowledge of the \( d_i \)'s can be related to the change in the symmetry coordinates \( D_i \)'s, from which the change
in internal coordinates can in turn be calculated.

The \( L \) matrix, which is the eigenfunction of the FG secular equations\(^{118} \), is a function of the vibrational frequencies and force fields, which are normally not available for the ionic states. However, it has been found that \( D \) is quite insensitive to \( L' \). Therefore, for the approximate work undertaken here, the \( L' \) matrix for the ion is approximated by that of the neutral molecule.

In addition, for simplicity, the vibrational wavefunctions are approximated by that of a harmonic oscillator, i.e.

\[
\phi_i = N_{v_i} H_{v_i}(\alpha_i, Q_i) \exp\left[-\frac{1}{2} \alpha_i^2 Q_i^2\right], \quad (2.2.35)
\]

in which

\[
N_{v_i} = \left(\alpha_i / \pi^{1/2} \right) \left(2^{v_i} v_i! \right)^{1/2},
\]

and

\[
\alpha_i^2 = 4\pi^2 c v_i / h.
\]

The \( H_{v_i}(\alpha_i, Q_i) \) are Hermite polynomials, \( v_i \) the vibrational quantum numbers, \( v_i \) vibrational frequencies in cm\(^{-1} \), and \( c \) is the speed of light. The component integral can then be expressed in the closed form\(^{119} \),
\[ M(v',v'') = K_{v',v''} \left( \frac{1-\beta^2}{1+\beta^2} \right)^{v'+v''/2} \sum_{\ell=0}^{\min(v',v'')} \left( \frac{4\beta}{1-\beta^2} \right)^\ell \cdot \]

\[ \frac{(-1)^v'}{\ell!(v'-\ell)!} \cdot \frac{v''}{(v''-\ell)!} \cdot H_{v',-\ell} \left[ i\beta^2 \gamma (1-\beta^4)^{-1/2} \right] \cdot \]

\[ H_{v''-\ell} \left[ -\beta^2 \gamma (1-\beta^4)^{-1/2} \right] , \quad (2.2.36) \]

where

\[ K_{v',v''} = (v'!v''!)^{1/2} \cdot 2^{-(v'+v''-1)/2} \cdot \frac{\beta^2 \gamma^2}{(1+\beta^2)^{1/2}} \cdot \exp\left[ \frac{(-1/2) \beta^2 \gamma^2}{1+\beta^2} \right] . \]

\[ [v',v''] \text{ designates the smaller of the two integers } v' \text{ and } v'', \]

and

\[ \beta = \alpha''/\alpha' , \quad \gamma = -\alpha'd . \quad (2.2.37) \]

Eq. (2.2.36) reduces, when \( v'' = 0 \), to

\[ M(v',0) = \frac{(-1)^v' 2^{1-v'}/2}{(v'!)^{1/2}} \cdot \left( \frac{\beta}{1+\beta^2} \right)^{1/2} \cdot \exp\left[ -\frac{1}{2} \frac{\gamma \beta^2}{1+\beta^2} \right] \cdot \]

\[ \left( \frac{1-\beta^2}{1+\beta^2} \right)^{v'/2} \cdot H_{v'} \left[ i\beta^2 \gamma (1-\beta^4)^{-1/2} \right] . \quad (2.2.38) \]
The main calculation is carried out by a computer program (Appendix) and the procedure is summarized:

1. \( d_i \) is set equal to zero for the vibrational mode not excited in the ion.

2. The FC factors (FCF) for any combination level are calculated as the product of those for the corresponding overtone levels.

3. For each excited vibration, the FCF are calculated at a series of \( d_i \) values. The best \( d_i \) value is then chosen on the basis of two criteria: (a) The overall qualitative features of the experimental FCF are followed in the calculated FCF. (b) The standard deviation of the calculated FCF from the experimental FCF is a minimum.

4. \( D_i \)'s are evaluated from the \( d_i \)'s.

5. The change in internal coordinates are calculated from the \( D_i \)'s.

6. Since the sign of each \( d_i \) is undetermined there are \( 2^N \) possible ionic state models consistent with the observed FCF, where \( N \) is the number of vibrational modes of the same symmetry excited. The choice of the model is based on the bonding character of the MO from which the electron is removed.

The method outlined above has been used wherever applicable in this study to estimate the geometry of the ions. By comparing with the experimental data, it will be shown (section 5.2.4) that this method is quite reliable in deter-
mining the ionic geometries, with a maximum deviation of 0.006 Å in bond lengths.

2.2.4 Selection Rules In PES

(a) Selection Rules In Electronic Excitations

It is usually assumed that the initial (neutral) and final (ionic) states are represented by single Slater determinants. The \(i^{th}\) photoionization process can then be described as the excitation of an electron from the orbital \(\phi_i\) to a continuum photoelectron orbital \(\phi_{ph}\). The transition probability for the process is proportional to the square of the electronic transition moment \(R_e\) (eq. (2.2.19)), and using the above assumption, we have,

\[
\text{Transition probability} \propto \left| \int \psi_e^i (N) R_e \psi_e^f (N) dq \right|^2
\]

\[
= \left| \int \phi_i R_e \phi_{ph} dq \right|^2 \left| \int \psi_e^i (N-1) \psi_e^f (N-1) dq \right|^2
\]

(2.2.39)

\[
= \left| \int \phi_i R_e \phi_{ph} dq \right|^2 \cdot \prod_{j \neq i} \left| \int \phi_j \phi_{ph} dq \right|^2
\]

(2.2.40)

where \(\psi_e^i (N-1)\) is the \(N-1\) electron remainder of the initial state function \(\psi_e^i (N)\) of an \(N\) electron molecule and \(\psi_e^f (N-1)\) is the wavefunction of the ion. The properties of the integrals in equations (2.2.39) and (2.2.40) dictate the following
selection rules on the difference between $\psi_e^i (N)$ (molecule) and $\psi_e^{f} (N-1)$ (ion).

(1) The change in the total spin angular momentum must be $\pm \frac{1}{2}$ due to the dipole matrix.

(2) The overlap integral in eq. (2.2.39) requires that the 'passive' orbitals have the same symmetry.

(3) In the frozen orbital approximation (KT), the overlap integral in eq. (2.2.40) requires that the ion and molecule differ only in one orbital.

In short, under the assumptions of the frozen orbital approximation and that the wavefunctions are described by single Slater determinants of one electron orbitals, photo-ionization is a single step one electron process, and the PE spectrum of a closed shell molecule may be assigned on the basis of one IP per orbital.

However, multi-electron (i.e. two or more) processes may be allowed if electron correlation is taken into account in the wavefunctions. The inclusion of electron correlation is usually accomplished by the method of configuration interaction (CI)\textsuperscript{120-125}, in that the ionic wavefunction is constructed as a linear combination of the configurations corresponding to the possible excited ionic states of the same symmetry, i.e.

$$\psi_j^{CI}(N-1) = \sum_i C_{ij}\psi_i^{f}(N-1).$$

(2.2.41)
The transition probability to a CI state is given by

\[ |\int \phi_i R e^{\phi_p d\eta} |^2 |\int \psi_e (N-1) \sum C_{ij} \psi_i^f (N-1) d\eta|^2. \] (2.2.42)

The overlap integral, and thus the transition probability will not be zero if the CI wavefunction contains at least one ionic state which is formed by a single electron process. For such a CI state the probability then reduces to

\[ |\int \phi_i R e^{\phi_p d\eta} |^2 |\int \psi_e (N-1) \psi_o^f (N-1) d\eta|^2 C_{i_0}^2, \] (2.2.43)

where \( \psi_o^f \) is the wavefunction of the allowed ionic state, and its value relative to that of the latter \( \psi_o^f \) is given by the square of their overlap integral, i.e.

\[ |\int \psi_o^f (N-1) \psi_i^f (N-1) d\eta|^2 = C_{i_0}^2. \] (2.2.44)

Qualitatively, multi-electron processes can be thought to occur due to perturbations induced by the photo-ionization process. Therefore, one would expect these processes to become more probable when more energetic ionic states are formed by using more energetic light sources. In practice this is what is observed. Thus multi-electron processes are quite common in ESCA\( ^1,^2 \) (>1000 eV), but exceptionally few have been claimed\(^ {125-127} \) to occur in HeI (21.22 eV) PES. However, two electron processes have recently been found
to occur quite frequently in HeII (40.8 eV) PES\textsuperscript{128}.

(b) Selection Rules In Vibrational Excitations

The selection rules in vibrational excitations are determined by the vibrational overlap integral (eq. (2.2.25)),

\[ M = \int \prod_{i=1}^{n} \phi'(Q_i^1) \prod_{j=1}^{n} \phi''(Q_j^2) dQ_1^1 dQ_2^2 \ldots dQ_n^1. \]

In order for \( M \) not be zero, the integral must be totally symmetric. Usually the initial state is a vibrationless ground state, whose vibrational wavefunction is totally symmetric. Hence the vibrational wavefunction of the ion must be totally symmetric as well. This requirement leads to the following selection rules\textsuperscript{129}.

(1) Totally symmetric vibrations may assume any quantum number.

(2) Non-totally symmetric vibrations can only assume zero or even quantum numbers, whose wavefunctions are then totally symmetric.

(3) For combination bands, i.e. simultaneous excitation of two or more vibrational modes, of non-totally symmetric modes, the transition is allowed if the total wavefunction is totally symmetric.

For a vibrationally excited initial state, the requirement that the overlap integral must be totally symmetric can be used to select the allowed transitions.
2.3 Linewidths And Resolution In PES

Like any other kind of spectroscopic measurements, the observed linewidth of a peak in PES is a convolution of the instrumental function and the inherent linewidth of the transition. The former is a measure of the instrumental resolution, while the latter is a function of the nature of the transition and the molecule under consideration. It is immediately obvious that the observed linewidth can only be reduced at the expense of the instrumental resolution, and if the latter has been reduced to the negligible limit, the observed linewidth will then be the inherent linewidth.

The inherent linewidth is determined through the Heisenberg uncertainty principle by the lifetime of the ionic state. Depending upon the lifetimes encountered, this may range from a line broadening of $10^{-7}$ eV for a fluorescent ionic state, up to 0.4 eV for a rapidly dissociating ionic state. Because the ultimate theoretical instrumental resolution obtainable is greater than 1 meV (see below), one may also consider the line structures which are comparable to this limit to be inherent linewidths. For complex molecules, the inherent linewidth may then include rotational envelopes, closely spaced unresolved vibrational structures, spin-orbit splittings, Jahn-Teller and Renner-Teller splittings.

In PES, the instrumental resolution is usually defined as $\Delta E_{1/2}/E$, where $\Delta E_{1/2}$ and $E$ are respectively the full width at half maximum (FWHM) and the kinetic energy of the
electrons, both measured in eV. However, it is customary to use simply \( \Delta E_{1/2} \) as a measure of resolution, and in general the FWHM of the argon doublet \( ^2P_{3/2}, ^2P_{1/2} \) is used as a universal test. The various possible factors that limit the ultimate instrumental resolution have been discussed in detail by Turner and Samson. In practice, the following are the most influential and pose the major problems.

1. The Doppler effect due to the thermal motion of the molecule and the velocity of the photoelectron - These two parameters couple to give the Doppler width according to the formula:

\[
\Delta E_{1/2} = 0.723(ET/M)^{1/2} \text{ meV}
\]  

(2.3.1)

where \( M \) is the molecular weight of the ion, \( T \) is the absolute temperature, and \( E \) the kinetic energy of the photoelectron. To give a better feeling for the magnitude of this broadening, \( \Delta E_{1/2} \) is plotted in Fig. 2 for various values of \( M \) as a function of electron kinetic energy and temperature. This broadening can be reduced by cooling the sample or using less energetic light sources, e.g. NeI instead of HeI to produce photoelectrons of lower energy. The Doppler width can, in principle, be completely eliminated by forming the sample into molecular beam and analyzing the photoelectrons ejected perpendicular to it.
(a) Doppler broadening as a function of electron energy for different M values at 300 K

(b) Doppler broadening as a function of temperature for different $E_{\text{kin}}/M$ values
(2) Linewidth of the light source due to self-absorption -

It has been shown that the common types of line broadening encountered in a light source such as natural, Doppler, pressure and stark broadenings are far too small (<10^{-3} eV) compared to that due to self-absorption for the HeI resonance line. The linewidth due to the latter increases with the pressure, the length of the discharge region, and that of the undischarged gas column. Surprisingly, the broadening does not seem to depend on the nature of the light source nor the diameter of the discharge capillary. Dependent upon the above factors, linewidth can vary from 1 meV up to 7 meV. The lower limit can be obtained at the lowest possible pressure by a microwave discharge, although at the expense of the available light intensity.

(3) Line broadening due to the inhomogeneity of the electrostatic and magnetic fields - This includes the effects due to the residual earth magnetic field, inhomogeneous analyzer surface potential, and the micropotentials on the apertures. The last effect is particularly important in the case of transient species, and is difficult to remedy.

However, if careful precautions are taken to eliminate or reduce these limiting factors, an ultimate resolution of ~1 meV is possible, which would be sufficient to resolve rotational structure in some cases. To date, the best instrumental resolution achieved has been between 4-7 meV with the argon doublet, however, a nominal resolution of 10-25 meV is
conveniently obtainable in most laboratories, this being considered as 'high resolution' PES (much above 30-40 meV is considered medium resolution).

Besides the experimental considerations, the working resolution can be improved by the analytical analysis of the raw data. The method is to eliminate the linewidth due to instrumental function by deconvolution\textsuperscript{133-137}. The success of deconvolution requires an accurate estimation of the instrumental function, and that the data has a favorable signal to noise ratio. This technique has been used successfully\textsuperscript{137} to recover the spin-orbit splitting in the $X^2\pi_g$ state of $O_2^+$, and the result is comparable to the very high resolution study\textsuperscript{132}. 
3.1 Introduction

During the course of this study, two spectrometers have been employed. The first system was used for the initial exploratory work and except for some notable modifications, its detailed features were described in Cornford's thesis. The experience gained through exhausting the capabilities of that unit has subsequently played a significant role in the development of the second system, which is the focus of this chapter.

3.2 General Design Considerations

One of the purposes of this study was to design and construct a photoelectron spectrometer that would be suitable for the study of transient species and reactive molecules. In the design of such a spectrometer, there are several significant considerations:
(1) The spectrometer must have a fast pumping system. This is essential since the species of interest here are either short lived or tend to decompose easily on contact with surfaces. By faster pumping and hence reducing the time between the photoionization region (ionization chamber) and the region where they are produced (transient species) or stored (reactive molecules), the greater the chance of successfully recording a PE spectrum. A useful additional feature is the short pump-down cycle of the spectrometer, which involves a shorter time elapse before the unit is again in operating condition after venting and servicing. A further bonus of the fast pumping system is a reduction in the build-up of deposits which may decrease the efficiency of the analysis system.

(2) The spectrometer should have a versatile sample inlet system and an easily accessible ionization chamber. The individual transient species that are of interest may be produced by one of several completely different methods, such as microwave discharge, pyrolysis etc, or may, for reasons of chemical reactivity, require the use of a specific material for the inlet system and sample holder. It is therefore of the essence that the spectrometer can handle all these differing situations. Easy access to the ionization chamber region is of particular importance, since most samples, by virtue of their short lifetimes or reactivity, must be generated as close to the chamber as possible.
(3) The spectrometer should have high sensitivity and the capability of high resolution (better than 25 meV). It is absolutely essential to have high sensitivity since more often than not the transient species are produced only with low partial vapor pressure, e.g. sometimes as low as 1% of the parent molecule. High resolution is necessary to resolve any fine band structure which is necessary for a rigorous analysis of the spectrum.

(4) The spectrometer should be as durable as possible with respect to corrosive vapors and yet as simple as possible in construction. It should also be easily assembled and dissembled so that cleaning, repairing and modifying become straightforward procedures.

(5) In addition to the earth's magnetic field, other magnetic fields may be introduced by certain experimental arrangements, e.g. by the current generated in a wire-wound furnace. The source of this field is usually so close to the electron trajectory in the analyzer, that it makes the magnetic shielding by Mu-metal infeasible. Consequently, the elimination of stray magnetic fields is best achieved by three pairs of Helmholtz coils mounted at right angles to each other. These may be individually adjusted to compensate for any such field effects.

(6) A minor, but equally important consideration is the siting of the spectrometer in a relatively field-free
room, with independent power supplies thus limiting the interference of other electrical apparatus.

3.3 The Spectrometer

3.3.1 The Vacuum System

The vertical cross-section of the spectrometer through the entrance and exit apertures of the electron analyzer is shown in Fig. 4. One distinct feature of the vacuum system is that it does not have a separate vacuum housing for the analyzer, in contrast to other conventional spectrometers. As a result, the ionization chamber is within easy access and the pumping volume is reduced considerably, a favorable condition for fast and efficient pumping. The ionization chamber and the analyzer are separated by the circular apertures in the ionization chamber, lens and entrance slit as shown in Fig. 4. The diameters of the apertures in the above-mentioned order are respectively 0.030", 0.100" and 0.020". The ionization chamber is connected through a 2" i.d. vacuum throttle valve (Varian Associates) to a 4" oil diffusion pump (Cooke Vacuum Prod., DP0 4-1000B) with a pumping speed of 1000 l/sec (air). The analyzer and the housing for the channel electron multiplier are pumped through a 1 5/3" i.d. vacuum throttle valve (Veeco forged brass angle valve, type SL 150S) by a 2" oil diffusion pump (ARC HS2) with
THE PHOTOELECTRON SPECTROMETER
VERTICAL CROSS-SECTION OF PE SPECTROMETER

Discharge tube

materials
- brass
- sapphire balls
- O-rings
- teflon

electron multiplier

lead
capillary tube light source
molecular beam inlet

mylar
lens system

4" Diffusion pump

2" Diffusion pump

FIGURE 4
PUMPING PORTS FOR THE ANALYZER UNIT AND GENERAL SAMPLE INLETS

Figure 5
a pumping speed of 285 l/sec (air). These diffusion pumps are respectively backed by Duo-Seal rotary pumps (Welch Scientific, model 1397 and 1402). The six pumping ports for the analyzer are shown in Fig. 5 and are arranged so as to have the least possible disturbance on the electron trajectory. These ports and the one for the multiplier housing are long cylinders of 3/8" in diameter drilled at an angle through the solid brass block which is also an integral part of the analyzer. An ionization gauge (NRC 538P) situated below these ports is used to measure the pressure of the system. The vacuum seals are effected by Viton O-rings, with the help of bolts wherever necessary.

3.3.2 The Electron Energy Analyzer

A 180° hemispherical electrostatic analyzer was selected for the spectrometer for the following reasons:

(1) The design of the vacuum system depends upon it.

(2) The ionization chamber can be readily accessible.

(3) An electrostatic analyzer was chosen over a magnetic analyzer because the energy (electrostatic) analysis is more straightforward than the momentum (magnetic) analysis in that the deflecting electric potential is a linear function of the electron energy. However, the magnetic analysis is convenient to use at relatively
high electron energies (≈10^4 eV, thus their use in ESCA is more popular).\textsuperscript{139,140}

The energy dispersion properties and focusing action of hemispherical electrostatic analyzers was first discussed by Purcell.\textsuperscript{141} It has subsequently been developed and its properties discussed by a number of researchers.\textsuperscript{142-146} A schematic diagram of the analyzer unit is shown in Fig. 6. The potential \( V_{12} \) applied between the two hemispherical surfaces of radii \( R_2 > R_1 \), produces at radius \( r \) a radial electrostatic field

\[
E(r) = \frac{A}{r^2}, \quad (3.3.1)
\]

and a potential

\[
V(r) = \frac{A}{r} + B, \quad (3.3.2)
\]

where \( A \) and \( B \) are constants. For an electron with a velocity \( v_0 \) which enters the analyzer at \( x_1 = 0 \) and at launch angle \( \alpha = 0^\circ \), and exits after being deflected by \( 180^\circ \), the following relationship holds,

\[
\text{Centrifugal force} = \text{Electric force}
\]

\[
\frac{m_e v_0^2}{R_0} = \frac{eA}{R_0^2} \quad (3.3.3)
\]
IONIZATION CHAMBER

LENS

\[ V_{12} \]

\[ V_R \]

\[ V_L \]

180° HEMISPHERICAL ANALYZER UNIT

FIGURE 6
If $eV_0$ in electron volts (eV) is set equal to the kinetic energy of the electron, $E_o = m_e v_o^2 / 2$, then

$$A = 2R_0 V_o = (R_1 + R_2) V_o ,$$  \hspace{1cm} (3.3.4)

where $R_o$ is the radius of the circle travelled by the electron. From eq. (3.3.2), the potentials of the inner and outer hemispheres with respect to $R_o$, which is also the midpoint, are then

$$V(R_1) - V(R_o) = A/R_1 - A/R_o , \hspace{1cm} (3.3.5)$$

$$V(R_o) - V(R_2) = A/R_o - A/R_2 , \hspace{1cm} (3.3.6)$$

and consequently $V_{12}$ is given by

$$V_{12} = V(R_1) - V(R_2) = A/R_1 - A/R_2$$

$$\hspace{2cm} = V_o [ (R_2/R_1 - (R_1/R_2)) ] . \hspace{1cm} (3.3.7)$$

In addition, for the hemispherical analyzer, other properties that are worthy of note include:
(1) The analyzer has first order angle ($\alpha$) focusing.

(2) The analyzer has two dimensional focusing because of spherical symmetry.

(3) Neglecting the $\alpha^2$ term, the energy resolution of the analyzer can be approximated by

$$\frac{\Delta E_{1/2}}{E_0} = \frac{w}{2R_0},$$

(3.3.8)

where $w$ is the diameter of the entrance and exit apertures.

The particular analyzer employed for the present spectrometer has the following parameters; $R_1 = 1''$, $R_0 = 1.25''$, $R_2 = 1.5''$ and $w = 0.020''$. Therefore the working conditions of the analyzer are

$$\frac{V_1}{V_2} = \frac{(+3)}{(-2)},$$

(3.3.9)

(eq. (3.3.5) and (3.3.6))

$$V_{12} = \frac{(5/6)}{V_0},$$

(eq. (3.3.7))

(3.3.10)

and

$$\frac{\Delta E_{1/2}}{E_0} = 0.8\%.$$ 

(eq. (3.3.8))

(3.3.11)

The outer and inner hemispheres of the analyzer were both machined from solid brass. The outer hemisphere is screwed to the supporting plate by four nylon screws and
is insulated by mylar and teflon spacers (Fig. 4). The inner hemisphere is held in position by three sapphire balls and is also screwed to the supporting plate, while its insulation is effected by the Viton O-ring and the teflon sheathing (Fig. 4). The hemispherical surfaces are gold plated and then coated with colloidal graphite (Crown, 8078 Dry Graphite Lubricant). This coating improves the experimental resolution considerably and also greatly reduces the background due to scattered electrons. Moreover, it acts as a protective coating for the hemispheres, since the analyzer efficiency can be completely restored after sample poisoning by removal of the old coating with an organic solvent and application of a new coating.

3.3.3 The Light Source Unit

The 584 Å HeI resonance line is produced by a low pressure microwave discharge in unpurified helium (Canadian Liquid Air) powered by a Microtron-200 Generator (Electro-Medical Supplies) with a maximum output of 200 watts at 2450 MHz. The microwave resonant cavity is of the type described by Zelikoff et al\textsuperscript{147}, and its design specifications were fully reported in Vroom's\textsuperscript{148} thesis. The characteristics of such a source have been described by Samson\textsuperscript{149}. While the 584 Å line is the most intense, small amounts of 537 Å (23.09 eV), 522 Å (23.3 eV) and 304 Å (40.8 eV) are also present in
the light source. In addition, the presence of impurity lines due to H\(\alpha\)(1215 Å), H\(\beta\)(1025 Å), NI(1134, 1200 Å) and OI(939, 1304 Å) is quite common, and frequently gives rise to extra bands in the PE spectra.

The vertical cross-section of the light source unit is shown in Fig. 7. The discharge is produced in a quartz tube (5 mm o.d.), the radiation emerging through a boron nitride constriction, into the collimating capillary tube (1 mm i.d.), and thence into the ionization chamber in a direction perpendicular to a line joining the entrance and exit apertures of the analyzer. The pumping port for the unwanted helium is also used for aligning the discharge tube and the capillary. The alignment is effected by constraining the two brass sheathings, one of which fits snugly over the discharge tube and the other over the capillary, into a linear configuration by the solid brass housing, and is further assisted by the Viton O-rings (Fig. 7), which also serve as vacuum seals. The undischarged helium is pumped either by a rotary or a 2" oil diffusion pump. However, the former has been found to be sufficient for the removal of excess He, thereby giving an efficient and intense source of HeI radiation. The more efficient diffusion pump is anticipated to be more effective for the production of the HeII line.
VERTICAL CROSS-SECTION OF THE LIGHT SOURCE UNIT

A. 180° HEMISPHERICAL ANALYSER
B. SUPPORTING PLATE
C. IONIZATION CHAMBER PUMPING PORT
D. IONIZATION CHAMBER
E. TEFILON
F. LENS
G. ENTRANCE APERTURE
H. O-RING SEAL
I. ALIGNMENT SHEATHING
J. COLLIMATING CAPILLARY (BRASS)
K. BORON NITRIDE CONSTRCTION
L. HELIUM PUMP OFF
M. SEALING FLANGE
N. TUNING STUB
O. FORCED AIR COOLING
P. MICROWAVE CAVITY
Q. POWER INPUT
R. QUARTZ DISCHARGE TUBE
S. QUARTER WAVE ADJUSTER
T. HELIUM INLET

FIGURE 7
3.3.4 The Sample System

(a) General Sample Inlet System

Stable samples are handled and stored in two separate but similarly constructed vacuum lines. Except for the one-litre glass storage flask, one of them is made of stainless steel and the other is of brass. Stainless steel or brass veeco angle valves are used in these lines for isolation purposes. A thermocouple (Varian HRC type 501) and a pressure gauge (Marsh type 3 2" Compound Gauge) in each line measure the vacuum and the sample pressure respectively. The control of the sample pressure into the ionization chamber is regulated by a variable leak valve (Granville Philips Series 203). The connection between the leak valve and the ionization chamber is made very flexible for simple disconnection by using 1/8" o.d. stainless steel or brass tubing and screw-on type O-ring vacuum seals (Fig. 5). This flexibility ensures lack of strain, and enables the various inlets to be set into any desired configuration.

(b) Direct Inlets For Reactive Molecules

The considerations for reducing the decomposition of reactive molecules before they are photoionized include:

(1) Choice of the right kind of material for the sample holder,
(2) Reduction in collisions with the walls, and hence
reduction in time between source and photoionization, and

(3) Cooling of the sample.

Three direct inlets, which are made of Kel-F, pyrex, and stainless steel respectively, have been constructed and used in this study, and they have been successful on all the occasions so far encountered. The configuration of the spectrometer when these units are in use is exemplified in the cases of the pyrex and Kel-F units, both shown in Fig. 8. When these units are used, the sample is held in the liquid or solid phase by immersing it in a suitable slush bath, and the operating sample pressure in the ionization chamber is controlled by the combined use of the 4" oil diffusion pump and the regulating valve (Kel-F, Teflon or stainless steel) (note - under such conditions the most volatile component comes off first, but by careful monitoring of the spectrum the course of the experiment can be followed.)

(c) Microwave Discharge Unit For Producing Transients

The configuration of the discharge apparatus is shown in Fig. 3. If necessary, the discharge cavity (Evenson type can be brought closer than 5 cm to the photoionization region (Fig. 9). The screw-on Viton O-ring vacuum seal is so designed that the discharge tube can be tilted as much as 15° to prevent stray electrons produced in the discharge
DIRECT SAMPLE INLETS

KEL-F INLET

PYREX INLET

FIGURE 8
MICROWAVE DISCHARGE ASSEMBLY

FIGURE 9
from going directly into the analyzer and causing high background counts. These stray electrons can further be reduced through collimation and enhanced wall collisions by inserting the discharge tube closer to the ionization chamber. By use of a nozzle (0.5 mm) in the discharge tube immediately above or below the discharge cavity, the production of the transient species can frequently be dramatically increased, as a result of the formation of a nozzle type molecular beam.

(d) High Temperature Pyrolysis Unit For Producing Transients

The components (the heater, the quartz and cooling units) of the pyrolysis unit are shown in Fig. 10. The 7 cm heater is made of 0.10" thick platinum wire noninductively wound on a grooved boron nitride (BN) thin-walled former, which fits snugly into another BN sheathing for positioning the wires and reducing heat loss. The quartz unit is made from two quartz tubes of 3 mm o.d. and 20 mm i.d. respectively, by sealing them at one end to form a nozzle. The other end of the outer tube is joined through a Kovar seal to the stainless steel vacuum-sealing flange which has three adjustable screws resting on the cooling unit for raising, lowering or tilting the quartz unit. The cooling unit is made of copper with an opening for differential pumping, and the cooling is effected by flowing cold water through it. The heater slides over the inner tube to sit at the bottom of the quartz unit, which in turn fits into the cooling unit. The whole assembly sits on the pumping port for the ionization chamber. All vacuum seals
are accomplished by Viton O-rings. The lengths of the quartz and cooling units are so chosen that the nozzle is just a few mm above the photoionization point. An Alumel-Chromel thermocouple for temperature measurement is inserted halfway up the BN heating unit. The power for the heater is supplied through a Variac from an ordinary 110 volt AC line. A steady temperature of 1200°C is obtained with 250 watts at 3 amps. Under these conditions, the temperature of the spectrometer is merely warm to the touch, indicating that the cooling is sufficient. A slight adjustment of the Helmholtz coil settings is all that is necessary to retune the spectrometer. However, it has been found necessary to tilt the heater a little by means of the 3 adjusting screws in order to reduce the large background counts which presumably arise from the thermally emitted electrons emerging directly into the analyzer.

(e) Variable Temperature Unit For Equilibrium Studies

The components (before being welded together) of the variable temperature unit are shown in Fig. 11. The heater, which is wound noninductively around the coiled stainless steel (s.s.) inlet tubing, is made of 0.013" non-magnetic chromel-P wires. The sample gas flowing through the s.s. tubing is cooled by cold nitrogen gas generated by vaporizing liquid nitrogen from a dewar, or heated by the heater wires, and its temperature is measured by an Alumel-Chromel thermocouple spot-welded onto the tubing. By controlling the cold nitrogen flow rate or the power supplied to the heater, the temperature of the sample can be varied between -180°C and 500°C, with a fluctuation of ±5°C. The
VARIABLE TEMPERATURE UNIT

- COLD $N_2$
- $N_2$
- SAMPLE IN
- THERMO-COUPLE
- HEATER
- COILED TUBING
- COOLER SHIELD
- NOZZLE UNIT
- TO IONIZATION CHAMBER

FIGURE 11
demountable nozzle is designed for the study of supercooled molecular jets. The unit sits on the pumping port of the ionization chamber, with the nozzle being about 2 mm above the photoionization point. The vacuum seal and insulation are again obtained by the Viton O-rings and the plexiglass washer.

3.3.5 The Scanning And Detecting System

The control circuitry for the spectrometer is shown in Fig. 12. For reasons of simplicity and economy, all voltages are supplied by the use of batteries, which are grounded on one side (except that for the analyzer). Voltage adjustments are accomplished using vernier-drive potentiometers (TRW Trimmers-Potentiometers). The power for each Helmholtz coil is supplied by a DC power supply (Lambda LH122A FM).

The analyzer can be operated in one of two possible scanning modes: (1) The potential difference \( V_{12} \) between the hemispheres is scanned, while keeping the ionization chamber at ground potential. (2) The potential difference \( V_R \) between the ionization chamber and the grounded entrance aperture of the analyzer is scanned, while keeping that between the hemispheres at a selected value. This selected value depends upon the desired resolution and intensity. The scanning potentials are respectively supplied by a programmable sweep (first mode) or by amplifying a 4 volt ramp originating from a multichannel analyzer (Fabritek 1072) (second mode), and their ranges can be respectively varied in steps of 0.1 volts or linearly up.
PE SPECTROMETER CONTROL

RAMP AMPLIFIER

FIGURE 12
to 20 volts. In the first scanning mode, electrons of different energies are successively focused and thus are analyzed at different resolutions (refer eq. (3.3.8)), while in the second mode, they are pre-accelerated or pre-decelerated to the selected focusing energy of the analyzer, and thus are analyzed at constant resolution.

A channel electron multiplier (Mullard B319AL) operating in saturated mode is used for electron detection. A positive voltage of $\sim 3000$ volts (Hewlett Packard 6525 DC Power Supply) is applied to its output while the input is held at 300 V above ground (by battery) to accelerate the electrons. Pulse counting is used for data acquisition and conventional pulse counting equipment is used for this purpose, namely, a preamplifier, an amplifier and a discriminator (Harshaw NA-15, NH-34A). The data readout system may involve a multichannel analyzer (Fabritek 1072), ratemeter (Harshaw NR-10), chart recorder (Hewlett Packard 680 Strip Chart Recorder) and X-Y plotter (MFE Plotamatic 715).

3.4 Operation And Performance Of The Spectrometer

The base vacuum is in the region of $1-3 \times 10^{-6}$ mm Hg, which can normally be obtained starting from atmospheric pressure in about one hour, provided that the system has not been exposed to the air too long for appreciable adsorption to have occurred. The helium gas in the light source hardly
increases the base pressure, since it is being differentially pumped (section 3.3.3). The pressure of the sample at the ionization chamber is not measured directly, but is instead monitored by the ionization gauge (section 3.3.1). The operating pressure as read at the ionization gauge is between $0.4-3 \times 10^{-5}$ mm Hg (ca. 0.01-1 Torr in the ionization chamber). The differential pump on the ionization chamber is isolated when stable samples are being run since large quantities of sample would be consumed, and is partially or completely opened for running reactive molecules or transients.

The advantages and disadvantages of operating the analyzer in the two scanning modes (section 3.3.5) are shown by recording the PE spectrum of oxygen in the respective mode (Fig. 13). In the first mode (scan $V_{12}$), very low energy electrons (0-2 eV) are badly discriminated against, with the result that the fourth band of $O_2$ can only be detected after applying a positive potential to the lens (Fig. 13), and variable resolution (linewidths) is obtained in the same spectrum because of the constant $\Delta E_{12}/E$ (eq. (3.3.8)). In the second mode (scan $V_R$), a rising background normally occurs on the low kinetic energy side, and occasionally is so strong to obscure any bands in this region. The second mode is superior in that very high resolution can be obtained by decreasing $V_{12}$, although at the expense of signal intensity, while the second mode may be used as a check that all bands are detected at fairly low electron energy region (1-4 eV). Consequently, in
a. SCAN $V_{12}$

lens = 80 volts

lens = 0 volt

b. SCAN $V_R$

IONIZATION POTENTIAL (eV)

FIGURE 13
practice, the analyzer is always operated in the second mode, with the energy of the focused electrons chosen to give the best compromise between resolution and intensity, and whenever necessary the second mode is used as a cross check. In the second scanning mode a negative lens at a selected potential, presumably due to its focussing action on the electrons, has been found to increase the intensity drastically and is thus always used.

As discussed in section 2.3, the major stumbling block to very high resolution is the inhomogeneous surface potential and micropotentials at the apertures. This is especially detrimental in the present study since the spectrometer is constantly exposed to corrosive or reactive vapors, making it extremely difficult to obtain the theoretical resolution (0.8%). The kind of resolution and sensitivity which is typical of the present spectrometer when it is relatively clean is given in Table 2, where is shown the observed half width of the Ar $^{2}P_{3/2}$ peak and its intensity at different focusing conditions. The best resolution obtained has been 15 meV with an intensity of 10,000 counts/sec. Normally the spectrometer is operated at a resolution of 20-30 meV with counts of ~30,000 per sec.

The potential of the present system for studying transient species is tested on some atomic species, e.g. H, N and F, and O$_2$ ($^{1}A_g$), which have been reported by Jonathan
TABLE 2*  FWHM and Intensity Of The Argon $^{2}P_{3/2}$ Peak at Different Focusing Conditions

<table>
<thead>
<tr>
<th>$\Delta E_{12}$</th>
<th>I</th>
<th>$E$</th>
<th>$V_{12}$</th>
<th>$V_{R}$</th>
<th>$V_{L}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(meV)</td>
<td>(counts/sec)</td>
<td>(eV)</td>
<td>(volt)</td>
<td>(volt)</td>
<td>(volt)</td>
</tr>
<tr>
<td>19</td>
<td>2,000</td>
<td>0.251</td>
<td>0.209</td>
<td>5.015</td>
<td>-0.065</td>
</tr>
<tr>
<td>20</td>
<td>6,000</td>
<td>0.370</td>
<td>0.303</td>
<td>4.326</td>
<td>-0.299</td>
</tr>
<tr>
<td>20</td>
<td>9,000</td>
<td>0.490</td>
<td>0.408</td>
<td>4.673</td>
<td>-0.428</td>
</tr>
<tr>
<td>20</td>
<td>11,000</td>
<td>0.607</td>
<td>0.506</td>
<td>4.523</td>
<td>-0.650</td>
</tr>
<tr>
<td>21</td>
<td>15,000</td>
<td>0.727</td>
<td>0.606</td>
<td>4.369</td>
<td>-0.754</td>
</tr>
<tr>
<td>22</td>
<td>19,000</td>
<td>0.847</td>
<td>0.706</td>
<td>4.220</td>
<td>-0.904</td>
</tr>
<tr>
<td>23</td>
<td>25,000</td>
<td>0.966</td>
<td>0.805</td>
<td>4.046</td>
<td>-1.124</td>
</tr>
<tr>
<td>24</td>
<td>29,500</td>
<td>1.085</td>
<td>0.904</td>
<td>3.907</td>
<td>-1.273</td>
</tr>
<tr>
<td>25</td>
<td>38,000</td>
<td>1.201</td>
<td>1.001</td>
<td>3.746</td>
<td>-1.426</td>
</tr>
<tr>
<td>30</td>
<td>43,000</td>
<td>1.321</td>
<td>1.101</td>
<td>3.597</td>
<td>-1.586</td>
</tr>
<tr>
<td>31</td>
<td>48,000</td>
<td>1.441</td>
<td>1.200</td>
<td>3.441</td>
<td>-1.726</td>
</tr>
</tbody>
</table>

* $\Delta E_{12}$: FWHM of the peak; I: Intensity; E: Energy of the focused electrons; $V_{12}$: Potential across the analyzer hemispheres; $V_{R}$: Retarding potential and $V_{L}$: Potential of the lens.
et al.\textsuperscript{44-47}. The PE spectra of these species are shown in Figs. 14, 15 and 16, and were obtained by a microwave discharge in the indicated molecules without the use of any diluent gas. In all cases, our results are at least comparable to those of Jonathan et al.\textsuperscript{44-47}, but with a significant improvement in resolution. This merit has enabled us to detect some new features in the PE spectra of CS (section 4.1) and SO(\textsuperscript{3}\Sigma^-) (section 4.2).
A)
DISCHARGE IN H₂

B)
DISCHARGE IN N₂

FIGURE 14
FIGURE 15

(A) DISCHARGE IN CF₄

(B) DISCHARGE IN SF₆

IONIZATION POTENTIAL (eV)
FIGURE 16

IONIZATION POTENTIAL (eV)

DISCHARGE IN O₂

O₂(3Σ⁻)
O₂(¹Δg)
O₂⁺(²Δg)
O₂⁺(²Φμ)
O₂⁺(3Σ⁻)
O₂⁺(²D)
O₂⁺(²P)
O₂⁺(⁴S)
O₂(Δg)
O₂(²Πg)
O₂(3Σ⁻)/537 Å

O₂(3Σ⁻) — O₂⁺(²Δg)
O₂⁺(3Σ⁻) — O₂⁺(2Δg)
CHAPTER FOUR

PHOTOELECTRON SPECTROSCOPY OF SOME TRANIENT SPECIES

4.1 Carbon Monosulfide (CS)

4.1.1 Introduction

Carbon monosulfide (CS) has been extensively studied by spectroscopic methods\textsuperscript{151}. The species can be produced in good yield by either the discharge or photolysis of CS\textsubscript{2}\textsuperscript{151g}. The first ionization potential (IP) of CS was reported by several groups using either electron impact\textsuperscript{152a}, mass-spectrometry\textsuperscript{152b} or conventional optical methods\textsuperscript{151j}. Very recently, two groups\textsuperscript{153} have obtained the photoelectron (PE) spectrum of CS giving the first two IP's. The first IP was identified\textsuperscript{153} as referring to the ground ionic state (X\textsuperscript{2}\Sigma\textsubscript{g}), and the second was tentatively assigned\textsuperscript{153a} to the ionic \textsuperscript{2}\Pi state.

Considering the similar electronic structure of CS to CO, we should expect each IP of CS to be lower than the
corresponding one of CO in view of the lower IP's of S than that of O. Therefore it is surprising that a third IP was not obtained by photoelectron spectroscopy. The PE spectrum of a neutral molecule resembles closely the electronic spectrum of the ion. It is instructive to compare the electronic states of CP, an isoelectronic species of CS⁺, with that of CS⁺. Two conclusions may be safely drawn. First, for CP, excited states A²Π and B²Σ are respectively 0.855 and 3.608 eV above the ground state X²Σ, while as for CS⁺, A²Π is 1.46 eV above X²Σ. The ordering of the first two electronic states of the two molecules are the same, and the separations are reasonably close. Hence it is reasonable to expect CS to have at least another IP below 21.22 eV. Secondly, the spin-orbit splitting for the 2Π state of CP is 158.3 cm⁻¹, and so the 2Π state of CS⁺ should have a spin-orbit splitting of a similar order of magnitude, probably larger. In the light of this, the reported spin-orbit splitting ¹⁵³a for the 2Π state of CS⁺ of ~30 cm⁻¹ seems rather small.

In the following, it will be shown that these expectations are indeed well borne out, and that the second IP can be unambiguously assigned to the 2Π state of the ion ¹⁵⁴.

4.1.2 Experimental

CS was produced by microwave discharge of CS₂. No attempt was made to remove CS₂ by trapping because no compli-
cations occurred due to its presence. Previously, we noticed the discharge in CS$_2$ was rather unstable and CS was produced in a measurable amount only for about an hour. A modified discharge cavity$^{155}$ which has been claimed to give better performance, was used instead. Great care was taken to ensure a very stable CS$_2$ pressure. Power as low as 50 W was found sufficient to produce maximum yield of CS. A quartz tube of 5 mm i.d. was used and the discharge cavity placed 27 cm from the ionization region. Under these conditions, a stable supply of CS with its first peak more intense than that of CS$_2$ was obtained continuously for six hours. Multiple scans for each IP of CS were possible. The spectra were recorded at a resolution between 25-30 meV (measured by FWHM of Ar peaks). Calibration was effected using the values for CS$_2$ which are in turn calibrated using argon.

4.1.3 Results and Discussion

The PE spectra of CS$_2$ with and without the discharge are depicted in Figs. 17a and 17b respectively. In addition to the two bands observed before$^{153}$, two more bands due to CS$^+$ are obtained. The IP's and the vibrational frequencies are collected in Table 3. Our values are in good agreement with the previous ones$^{153}$.

If an orbital description of the electronic structure is assumed, CS has a configuration
1b. M.W. DISCHARGE IN $\textbf{CS}_2$

![Graph showing ionization potential for $\textbf{CS}_2$ with peaks at different eV values.](image)

1a. $\textbf{CS}_2$

![Graph showing ionization potential for $\textbf{CS}_2$ with a peak labeled Ar.](image)

**FIGURE 17**
### TABLE 3 PES and Theoretical Data of CS

<table>
<thead>
<tr>
<th>Ionic state</th>
<th>Ionization potentials (eV)</th>
<th>Vibrational frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PES(^a))</td>
<td>Theoretical</td>
</tr>
<tr>
<td></td>
<td>This work(^b))</td>
<td>CND0/2(^d)) Ref. 158</td>
</tr>
<tr>
<td>X(^2\Sigma)</td>
<td>11.34</td>
<td>11.10 12.80</td>
</tr>
<tr>
<td>A(^2\Pi)</td>
<td>12.78 (12.90)</td>
<td>11.24 12.61</td>
</tr>
<tr>
<td>Ρ(^2\Sigma)</td>
<td>15.33 (16.06)</td>
<td>16.56 13.83</td>
</tr>
<tr>
<td>C(^2\Sigma)</td>
<td>18.03</td>
<td>24.64 30.12</td>
</tr>
</tbody>
</table>

---

a) adiabatic IP's are given, vertical IP in parentheses.
b) estimated experimental error ± 0.02 eV.
c) estimated experimental error ± 30 cm\(^{-1}\).
d) with 4 eV adjustment.
The four observed bands will then correspond to the removal of electrons from three $\sigma$ and one $\pi$ molecular orbitals (MO).

The spin-orbit splitting for the second band is resolved clearly (Fig. 18b) and has a value ($A$) of 280 ± 30 cm$^{-1}$. This value is in excellent agreement with a very recent result$^{156}$ (301.283 cm$^{-1}$) obtained from the electronic spectrum of CS$^+$. This then leaves no doubt that the second band corresponds to the $^2\Pi$ state and the other three to the $^2\Sigma$ states of CS$^+$.

The first band, giving a coincident adiabatic and vertical IP at 11.34 eV, has at least three observable vibrational components (Fig. 18a). The sharpness of the first peak, together with the increase in the vibrational spacing compared to the ground molecular state, i.e. from 1275 to 1380 cm$^{-1}$, indicates ionization of an antibonding $\sigma$ MO.

The second band (Fig. 18b) overlaps with one from CS$_2$. Because of the difference in vibrational spacings and the splitting of fine structure for CS, we are able to determine the adiabatic and vertical IP's accurately. This band has a vibrational series of at least six components, and the decrease in the vibrational spacing, together with the length of the series clearly indicates the removal of a
FIGURE 18

2c $\omega = 868 \text{ cm}^{-1}$

2a $\omega = 1384 \text{ cm}^{-1}$

2b $\omega = 972 \text{ cm}^{-1}$

2d $\omega = 1055 \text{ cm}^{-1}$

$A = -280 \text{ cm}^{-1}$
strongly bonding (\(\pi\)) electron.

The third band (Fig. 18c) is also overlapped by one from CS\(_2\). The resolution is good enough to enable an accurate determination of the adiabatic and vertical IP's at 15.83 and 16.06 eV respectively. The band shows at least six vibrational components and a large decrease in vibrational spacing. The MO involved appears to be even more bonding than the second.

The decrease in the vibrational spacing of the fourth band is in line with the removal of a bonding electron, yet the sharpness of the first peak (Fig. 18d) is unexpected. The corresponding IP has not been obtained for CO, but a fourth IP at 23.60 eV for N\(_2\) has recently been obtained from Rydberg series\(^{157}\). Hence by comparing with N\(_2\), it is reasonable to assign the fourth band, with an identical adiabatic and vertical IP at 18.03 eV, to the C\(^2\Sigma\) state of the ion.

In order to obtain more confirmation for the assignment, we resort to theoretical calculations. An ab initio SCF-LCAO-MO calculation using an extended basis set of Slater type orbitals\(^{158}\) has been carried out for CS. By applying Koopmans' theorem\(^{49}\), the IP's are calculated (Table 3). The agreement between the experimental and theoretical results is not satisfactory, notably in the ordering of the ionic \(\Pi\) state. This points to the fact that Koopmans' theorem must be applied cautiously. Never-
theless, the bonding character of individual MO's agrees with the experimental finding. We have performed a CIIIDO/276 calculation and surprisingly the predicted IP's are in better agreement with experiment, except that a bonding electron is indicated to be involved in the first IP.

4.2 Sulfur Monoxide (SO)

4.2.1 Introduction

The PE spectrum of SO\(^{3\Sigma^-}\) has been studied by Jonathan et al.\(^{47,159}\), who identified three IP's below 21.2 eV. It is clear that the spectrum of SO is far from complete and raises several points that need to be clarified. First, considering the similarity in electronic structure between \(O_2\) and SO, one notes that the reported spectrum of SO\(^{159}\) is far too simple in that some ionic states accessible in HeI PES may have been undetected. Secondly, the \(X^2\Pi\) ionic state should have a spin-orbit splitting greater than that of \(O_2^+ X^2\Pi_g\) state \((A = +195 \text{ cm}^{-1}\)^\(^{111}\)) and at least comparable to that of \(CS^+ A^2\Pi\) state\(^{160}\) \((A = -280 \text{ cm}^{-1}\), section 4.1.3). Therefore, with better resolution one should be able to resolve this splitting. Thirdly, in the study of \(S_2O\)^\(^{161}\) (section 4.3.3), we have raised the point that the 'second IP' of SO at 11.3 eV may be due instead to the second PE band of \(S_2O\). The present section is aimed at
attempts to answer these important questions.

4.2.2 Experimental

SO(2e-) was produced by a MW discharge (100W) in SO₂ without or with the addition of varying amounts of sulfur vapor. The amount of the latter was controlled by a heating tape wound around a side-arm of the discharge tube into which some (sublimed) sulfur powder was placed. The PE spectrum was calibrated using the spectroscopic IP's of the oxygen atoms produced in the discharge.

4.2.3 Results and Discussion

The PE spectra of SO₂(A) and the products of the discharge in SO₂ with different amounts of S vapor is shown in Fig. 19, with the amount of S increasing from B to J. The discharge in SO₂ alone gave a PE spectrum (Fig. 19B) which shows, in addition to the O⁺ peaks, two additional bands due to SO₄⁷,⁵⁹ at 10.33 eV and 14.94 eV. The spectrum is identical to that of Jonathan et al, except that the PE band at 11.3 eV is hardly detectable in Fig. 19B. With a little S vapor added into the discharge (Fig. 19C), the peaks due to O⁺ disappeared. In addition, two new bands at 10.6 eV and 11.3 eV began to appear, and they increased dramatically with respect to those of SO⁺ with increasing S vapor pressure (Fig. 19D). Moreover, at high S vapor pressure two more bands at 14.7 eV and 16.0 eV (Fig. 19D) could be
identified. Comparing with the PE spectrum of $S_2O$\textsuperscript{161} (section 4.3.3), these four bands can be assigned unambiguously to those of $S_2O$. This thus confirms our previous claim\textsuperscript{161} that the 2\textsuperscript{nd} band (11.3 eV) of SO observed by Jonathan et al\textsuperscript{159} was actually the 2\textsuperscript{nd} band of $S_2O$, which was formed by the reaction of SO with S deposited on the walls. The partial overlap of the first band of SO by that of $S_2O$ explains the unexpected broadening\textsuperscript{159} of $v' = 1$ and 2 peaks of the former.

The observation that the intensities of the bands of $S_2O$ grow with increasing S concentration is in complete accord with the fact\textsuperscript{163} that SO ($^3\Sigma^-$) formed in the discharge reacts rapidly with S to form $S_2O$. Indeed, with less efficient pumping SO can be eliminated from the spectrum as a result of its complete reaction with S.

The 1\textsuperscript{st} band of SO was recorded at high resolution and is shown in Fig. 20. The expected spin-orbit components are clearly resolved, with an average splitting of $320 \pm 20$ cm\textsuperscript{-1} (40 meV) which then leaves no doubt that the 1\textsuperscript{st} IP is due to the $2\Pi$ ionic state. The IP's and vibrational frequencies corresponding to the two distinct bands at 10.33 eV and 14.94 eV are collected in Table 4, and these values are in good agreement with the previous results\textsuperscript{47,159}.

The average total half-widths of the overlapped ($^{2\pi}_{1/2}, ^{2\pi}_{3/2}$) peaks in the 0-0 and 0-1 components of the $X^2\Pi$ state are $85 \pm 3$ meV. Using the observed spin-orbit splitting and assuming the peaks of the two spin states $^{2\pi}_{1/2}$ and $^{2\pi}_{3/2}$ are equally intense, have the same half-widths, and are of
$X^2 \Pi \frac{1}{2}, \frac{3}{2}$

$A = +320 \text{ cm}^{-1}$
<table>
<thead>
<tr>
<th>Ionic state</th>
<th>Vertical IP (eV)</th>
<th>(adiabatic) Vibrational frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This work</td>
<td>Ref. 159</td>
</tr>
<tr>
<td>(X^2\Pi_{\frac{1}{2}}, \frac{3}{2})</td>
<td>10.33±0.01</td>
<td>10.32</td>
</tr>
<tr>
<td>(a^4\Pi)</td>
<td>10.37±0.01</td>
<td>1270±30</td>
</tr>
<tr>
<td>(A^2\Pi)</td>
<td>13.90 (13.39)±0.10</td>
<td>--</td>
</tr>
<tr>
<td>(b^4\Sigma^-)</td>
<td>14.94±0.01</td>
<td>14.96</td>
</tr>
</tbody>
</table>
gaussian type, the half-widths of these individual peaks can then be estimated to be $54 \pm 4$ meV. This value is significantly larger than the observed half-widths of the peaks in the band at 14.94 eV, which are $45 \pm 3$ meV. The smaller half-widths of the latter tend to suggest that this band is probably due to a state with no spin-orbit splitting, i.e. a $\Sigma$ state (or a $\Pi$ state with a very small spin-orbit splitting which is unlikely in view of the 40 meV splitting for the $X^2\Pi$ state). Comparing with $O_2^{132}$, the assignment of this band to the $b^4 \Sigma^-$ state of $SO^+$ is most probable, as suggested previously.

Comparing the 13.5 - 15.0 eV region of the PE spectrum (Fig. 21) recorded with (B) and without (A) the MW discharge in $SO_2$ alone, we have observed that there are extra peak intensities and some additional peaks in the former. These features were also evident in the spectra measured by Jonathan et al. but had not been mentioned in their discussion. While the 2$^{nd}$ band of $SO_2^+$ (Fig. 21A) drops to the baseline beyond 14.1 eV, there are, however, some distinct peaks (Fig. 21B) in the same region which seem to correlate with the presence of $SO$ in the spectrum.

By manually subtracting the intensity of the 2$^{nd}$ band of $SO_2^+$ from the spectrum of the discharge products, the extra peak intensities are shown as vertical lines in Fig. 22. These peaks must then be due to $SO$ since their intensities follow the other bands of $SO$. The spacing between peaks varies between 850 cm$^{-1}$ and 700 cm$^{-1}$ with an average.
FIGURE 21
of 750 cm\(^{-1}\) compared with the ground state value of 1111 cm\(^{-1}\). The drastic reduction in vibrational frequency and the length of the progression (at least ca. 12 components) is indicative of the removal of a strongly bonding electron. By comparing with \(O_2^{+132}\), it seems reasonable to assign this band to be due to the \(a^4\Pi\) state, since the corresponding transition in \(O_2\) also shows an extensive vibrational progression with a large decrease in the vibrational frequency, from 1780 cm\(^{-1}\) to \(\approx 900\) cm\(^{-1}\) (for the molecule and ion). The adiabatic and vertical IP's of this band are estimated to be at 13.39 eV and 13.90 eV (\(v' = 5\)) respectively. Because of the overlap from the second band of \(SO_2^+\), these quoted IP values may be in error by as much as one vibrational quantum.

Upon close examination, it is noted that peaks of the \(a^4\Pi\) state broaden at and beyond \(v' = 6\), and irregular structure appears around 14.6 eV (Fig. 22). In view of the fact that this is reproducible and follows the SO band intensities, and guided by the spectrum of \(O_2^{+132}\), where a similar phenomenon occurs on the high energy side of the \(a^4\Pi_u\) band, we are inclined to suggest there may be an additional band in the mentioned region, which overlaps strongly with the \(a^4\Pi\) state of \(SO^+\). If this is genuine, it will then be the \(A^2\Pi\) ionic state. The corresponding adiabatic and vertical IP's cannot be determined with certainty but are estimated to be at 14.0 eV and 14.6 eV respectively (Fig. 22) and the
FIGURE 22

Ionization Potential (eV)

SO$_2^+$

O$^+$($^4S$) ×4

A$^2\Pi$ (?)

b$^4\Sigma^-$
vibrational spacing is approximately 700 cm$^{-1}$ compared with 1111 cm$^{-1}$ for the ground state. This compares with the values of 1780 cm$^{-1}$ and $\approx$800 cm$^{-1}$ for the $A^{2}\Pi_{u}$ state of $O_{2}$.

With the identification of the $a^{4}\Pi$ and $A^{2}\Pi$ states, the PE spectrum of $SO^{+}$ then, as expected, closely resembles that of $O_{2}^{+}$ except for the absence of the $B^{2}\Sigma_{g}^{-}$ state in the former ($O_{2}^{+}, 20.4$ eV). We suspect this state to be buried underneath the intense third band of $SO_{2}^{+}$ (at 16.6 eV).

In conclusion, it may be added that attempts to remove $SO_{2}$ from the discharge products either by selective cold-trapping or by using an excess of $S$ vapor resulted in the complete disappearance of $SO$ as well.

4.3 Disulfur Monoxide ($S_{2}O$)

4.3.1 Introduction

The chemistry of $S_{2}O$ has been reviewed by Schenk and Steudel. In the vapor phase and at low pressures of ca. one torr or less, $S_{2}O$ can be stable for a few hours, and SO formed as an intermediate in a reaction is almost always the precursor of $S_{2}O$\textsuperscript{163}. Historically, $S_{2}O$ was actually mistaken for SO for more than a decade until its identity was finally established in 1956.

The PE spectrum of $S_{2}O$ is, moreover, of additional interest because it is isoelectronic with the molecules $NSF$ and $SO_{2}$, the PE spectra of which have recently been the
subject of extensive studies \textsuperscript{167}-170. The related compound 
\textit{NSCl} has also been investigated\textsuperscript{167} because of disagreements
regarding the assignment of various ionization potentials\textsuperscript{168,169}. 
It will be shown that our results and assignments lead to a 
resolution and definite confirmation of the order of the orbitals 
in this series of molecules.

4.3.2 Experimental

\textit{S}_2\text{O} was produced by two separate methods.

(1) By the microwave discharge of sulfur dioxide (\textit{SO}_2) 
in the presence of sulfur, which was coated on the wall of 
the discharge tube. Depending on the pressure of \textit{SO}_2, 
various proportions of \textit{S}_2\text{O}/\textit{SO}_2 could be obtained. At a 
certain pressure, the PE spectrum of \textit{SO}_2 disappeared completely, 
yet when the supply of \textit{SO}_2 was turned off, the bands due 
to \textit{S}_2\text{O} also disappeared.

(2) By passing thionyl chloride (\textit{SOCl}_2) vapor through a 
4 cm column of silver sulfide (\textit{Ag}_2\text{S}) powder heated to about 
150$^\circ$C\textsuperscript{171}. The heater was made by winding chromel-P wires 
non-inductively around a quartz tube. The direct inlet system 
made of pyrex (section 3.3.4.b) was used for \textit{SOCl}_2 because 
of its ready decomposition. The PE spectrum of \textit{SOCl}_2 
disappeared completely when \textit{Ag}_2\text{S} was heated and the new bands 
appeared could be identified as due to \textit{S}_2\text{O} and \textit{SO}_2. The 
best yield was obtained at around 150$^\circ$C.

The PE spectra obtained from the two methods were
identical except for a difference in the $S_2O/SO_2$ intensity ratio, with the second method giving consistently better yields of $S_2O$ as expected\textsuperscript{163}. This leaves no doubt that the new species we observed is $S_2O$.

The resolution as measured by the FWHM of the argon $2p_{3/2}$ peak is between 25-30 meV. Calibration of the spectrum was effected using argon and oxygen. The estimated error is ± 20 meV for ionization potentials (IP's) and ± 30 cm$^{-1}$ for vibrational frequencies.

4.3.3 Results and Discussion

The PE spectrum obtained by passing $SOCl_2$ over heated $Ag_2S$ is shown in Fig. 23, where the PE spectra of pure $SO_2$ and $SOCl_2$ are also included for comparison. Although it was not possible to get rid of $SO_2$ from the spectrum of $S_2O$, fortunately its existence caused little problem. The PE spectrum of $S_2O$ (Fig. 23b) consists of four distinguishable bands with vibrational fine structure resolved in two of them. The IP's and vibrational frequencies are collected in Table 5.

The interpretation of the PE spectrum of $S_2O$ is aided by comparison with those of NSF\textsuperscript{167-170} and $SO_2$\textsuperscript{172}, which are isoelectronic to $S_2O$. Comparison with the PE spectra of NSCl\textsuperscript{167} is also helpful, since this has similar valence electronic structure to $S_2O$. The deductions drawn from these intermolecular comparisons and the MO calculations
FIGURE 23

(a) $SO_2$

(b) $SOCl_2$ over hot $Ag_2S$

(c) $SOCl_2$

Ionization Potential (eV)

Arbitrary Counts / sec
TABLE 5 PES and Theoretical Data for $S_2O$

<table>
<thead>
<tr>
<th>MO symmetry</th>
<th>IP$^a$ (eV)</th>
<th>IP$^b$ (eV)</th>
<th>IP$^c$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a'</td>
<td>9.68</td>
<td>10.53</td>
<td>480 (679)</td>
</tr>
<tr>
<td>6a'</td>
<td>10.36</td>
<td>11.25</td>
<td>930 (1165)</td>
</tr>
<tr>
<td>2a''</td>
<td>10.71</td>
<td>11.31</td>
<td>940 (1165)</td>
</tr>
<tr>
<td>5a'</td>
<td>14.11</td>
<td>14.3 (14.7)</td>
<td>----</td>
</tr>
<tr>
<td>1a''</td>
<td>14.13</td>
<td>14.9</td>
<td>----</td>
</tr>
<tr>
<td>4a'</td>
<td>15.44</td>
<td>15.5 (16.0)</td>
<td>----</td>
</tr>
<tr>
<td>3a'</td>
<td>18.39</td>
<td>18.7 (?)</td>
<td>----</td>
</tr>
</tbody>
</table>

a) IP's obtained by subtracting 4 eV from the corresponding absolute MO energy.
b) vertical IP's are in parentheses.
c) values in parentheses are the corresponding vibrational frequencies in the neutral molecule from ref. 166.
(see below) suggest six to seven accessible IP's and that the orbital configuration of \( S_2O \) is

\[
\text{KKKLL} (1a')^2(2a')^2(3a')^2(4a')^2(1a'')^2(5a')^2(2a'')^2
(6a')^2(7a')^2.
\]

In addition, the calculation shows, provided Koopmans' theorem holds, for \( S_2O \) the second and third IP's are close, and the fourth and fifth IP's are degenerate within experimental accuracy. The fact that the second and third IP's of \( SO_2 \), \( NSF^{168-169} \) and \( NSC^{167} \) are close and the fourth and fifth IP's of \( SO_2 \) are also close leads one to expect similar behavior from \( S_2O \), and lends support to the MO calculations. In fact, the PE spectra of these compounds are remarkably similar, as exemplified in the ionization potential correlation diagram depicted in Fig. 24. Namely, the PE bands of each compound can be grouped into three regions, i.e. the first IP, the second and third IP's, and the higher IP's. Consequently, the analysis for the spectrum of \( S_2O \) appears to be fairly straightforward using this intermolecular correlation. In order to strengthen the basis of the above expectation and to obtain more information for the analysis, we turn to MO calculations. A CNDO/2 MO calculation\(^7\) was performed on \( S_2O \) with the experimental geometry\(^1\) and the results collected in Table 5. The deductions from the intermolecular comparisons and the MO calculations are encouragingly consistent, and thus lend support to the MO calculation. Furthermore, the success with which the earlier approximate MO calculations predicted the
FIGURE 24
IP's of NSF, NSC and SO makes it evident that we can affect similar success in the case of S\(_2\)O.

The first band in the PE spectrum of S\(_2\)O (Fig. 25) consists of one IP, with the adiabatic and vertical values at 10.53 and 10.59 eV respectively. This is compared to 10.3±0.1 eV, the only observed IP of S\(_2\)O, obtained from mass spectrometry. The four clearly discernible vibrational components with an average spacing of 430 cm\(^{-1}\) are assigned to \(\nu_3\) which is mainly the S-S stretch. The calculation indicates the 7a' MO is S-S bonding in accord with the decrease of the vibrational frequency from 679 cm\(^{-1}\) in the neutral molecule to 480 cm\(^{-1}\) in the \(X^2A'\) ionic state. The assignment of the vibration 480 cm\(^{-1}\) to the bending mode \(\nu_2\) (338 cm\(^{-1}\) in the neutral molecule) is ruled out because the Walsh rules predict an increase in bond angle accompanying the removal of orbital 7a' and hence a decrease in bending frequency (as occurred in S\(_2\)O and NSF). However, the shape of the high energy end of the band may indicate an additional, but very weak vibrational progression of spacing ca. 200 cm\(^{-1}\), which if real should be the ionic bending frequency.

It is difficult to decide whether one or two IP's are involved in the second PE band (Fig. 25). As discussed above, we prefer to assign two IP's to this band and propose that electrons from the MO's 6a' and 2a'' respectively are removed. The corresponding IP's and vibrational frequencies are summarized in Table 5. The vibrational structure on
\( \nu_1 = 930 \text{ cm}^{-1} \)

\( \nu_2 = 480 \text{ cm}^{-1} \)

Ionization Potential (eV)

FIGURE 25
both bands seems to be a simple series in $\nu_1$, which is mainly S-O stretch, indicating a decrease in frequency in the ionic state. This is supported by the calculation, which predicts that the 6a' and 2a'' orbitals are, respectively, bonding and slightly bonding between the central S and the O atoms, while they are both bonding between the S atoms.

The third and fourth bands are both broad and featureless. The former starts at 14.3 eV and has its maximum at 14.7 eV, while the corresponding values for the latter are 15.5 and 16.0 eV respectively. Hagemann gave the appearance potential of SO from S$_2$O to be $< 14.5 \pm 0.2$ eV. This is consistent with the featureless character of the third band. Unequivocal assignment of these two bands is difficult. The CNDO/2 result is used for the tentative assignment, i.e. the third band arises from two IP's (MO's 5a' and 1a'') and the fourth from one IP (MO 4a'). The shape of the third band (Fig. 23b) suggests a fourth IP at 14.3 eV and a fifth at 14.9 eV. This then leaves one IP (predicted by calculation) unaccounted for, which we suspect to be part of the fourth band or at ~18.7 eV, where there is some indication of an additional band sitting on the rising background.

In the spectrum of S$_2$O obtained from the MW discharge of SO$_2$, in addition to the bands described above, we observed a clearly discernible vibrational series of three components with an averaging spacing of 920 cm$^{-1}$, corresponding to an
adiabatic and vertical IP at 14.95 eV. This band can be assigned unambiguously to be the third band of SO\(^+\) because of the close agreement of IP and frequency values with those found by Jonathan et al\(^{159}\) for SO\(^+\) as well as the similar experimental conditions. Furthermore we wish to point out that the assignment of the weak band at 11.3 eV by Jonathan et al\(^{159}\) to SO may not be certain. Considering that \(S_2O\) is invariably formed in the discharge of \(SO_2\)\(^{163}\) and the intensity of the second band of SO\(^{159}\) is seemingly incompatible with that of the other two bands, we would suggest that this is actually the second band of \(S_2O\), which we find to have its origin at very nearly the same energy, i.e. 11.23 eV. The first band of \(S_2O\) may very well be buried underneath the first band of SO in the spectrum of Jonathan et al (see also section 4.2.3).

4.4 Diazene (HN=NH) And Diazene-\(d_2\) (DH=ND)

4.4.1 Introduction

The short lived species HN=NH (or \(N_2H_2\)) has recently provoked a great deal of interest with regard to its chemistry\(^{175-177}\) and its spectroscopic properties\(^{178-185}\). \(N_2H_2\), as the first member of the azo series, has also attracted the attention of many theoreticians\(^{186-189}\). With this wealth of interest on the molecule, it thus seems surprising that \(N_2H_2\) remains a spectroscopic enigma in many respects, e.g. the intensity alternation in the vacuum
ultraviolet spectrum\textsuperscript{181}, the uncertainty in the precise interpretation of near ultraviolet spectrum\textsuperscript{184}, the geometry of the excited states, and the possibility of cis/trans isomerism in the gas phase.

In view of these controversies and the potential of PES in providing information on the electronic structure of molecules, it therefore seemed appropriate to undertake a PE study of $\text{N}_2\text{H}_2$.

The properties of $\text{N}_2\text{H}_2$ which are relevant to our studies here may be summarized as follows. It is generally accepted that the molecule in its ground state assumes a trans form and is a singlet electronic state, although a triplet ground state has been suggested\textsuperscript{181}. The molecule has a lifetime of the order of minutes in the vapor phase at low pressure, and decomposes rapidly to give $\text{N}_2$ and $\text{H}_2$ as major products.

4.4.2 Experimental

$\text{N}_2\text{H}_2$ was generated by two different methods.

1. A very weak microwave discharge\textsuperscript{177} in the equilibrium vapor of $\text{N}_2\text{H}_4$ (Eastman, 99\% purity) at room temperature. The PE spectrum of $\text{N}_2\text{H}_4$ (Fig. 26a) was essentially that of previous workers\textsuperscript{190}. Undissociated $\text{N}_2\text{H}_4$ and involatile products were trapped at $-78^\circ$C, the only remaining species in the gas phase being $\text{N}_2\text{H}_4$, $\text{NH}_3$, $\text{N}_2$ and $\text{H}_2$ (Fig. 26b). Great trouble was experienced by other workers due to the
presence of the \( \text{NH}_3 \), which may confuse any spectroscopic measurement, and indeed partly obscures the PE spectrum of \( \text{N}_2\text{H}_2 \) (Fig. 26b). Distillation, or trapping and revolatilization of the \( \text{NH}_3/\text{N}_2\text{H}_2 \) mixture does not alleviate this problem. However, we have eliminated this problem by titrating the gas phase products with HCl after passage through the trap at \(-78^\circ\text{C}\).

(2) The second method involved preparation of sodium bis(trimethylsilyl)amide from hexamethyldisilazane\(^{191,192}\). This, in turn, was converted into sodium tosylhydrazide by reaction with tosylhydrazine\(^{175}\). The sodium tosylhydrazide was then pyrolyzed at 55-60°C (as recommended by Wiberg et al\(^{175,176}\)) to give pure \( \text{N}_2\text{H}_2 \) plus \( \text{N}_2 \) and a little \( \text{H}_2 \) in the gas phase. However, we have found that by raising the temperature to 90-100°C and using faster differential pumping, the yield of \( \text{N}_2\text{H}_2 \) can be improved several fold with respect to \( \text{N}_2 \).

In both cases (1) and (2), the gas phase mixture of \( \text{N}_2\text{H}_2/\text{N}_2/\text{H}_2 \) was led directly into the ionization chamber, which was differentially pumped. The pressures registered at the ionization gauge were \( 2\times10^{-5} \) and \( 0.3\times10^{-5} \) mm Hg respectively in cases (1) and (2). Because of the much lower sample pressure in the latter, a long scanning time (\( \approx 1 \) hr) was necessary to record a decent spectrum. The PE spectra were identical in both cases except for a better \( \text{N}_2\text{H}_2/\text{H}_2 \) ratio in the 2\(^{nd}\) method.

\( \text{N}_2\text{D}_2 \) was generated from \( \text{N}_2\text{D}_4 \) (Merck, Sharp and
Dohme) by method (1) above. ND₃ was eliminated by gas phase titration with DCl.

In the discharge method outlined above the efficiency of the discharge in selectively producing N₂H₂/N₂D₂ could be monitored by trapping all the products at -196°C, and observing the yellow color of the diazene. In this respect, we have confirmation of the production of the desired species, the alternative preparative method for N₂H₂ providing us with further evidence for correct identification.

The spectra were calibrated using the IP's of the H₂, H₂/D₂ or HCl/DCl, with an accuracy of ± 0.01 eV for the IP's of sharp peaks and ± 30 cm⁻¹ for the vibrational spacings. Resolution in all cases was better than 30 meV.

4.4.3 Results

Fig. 26 depicts the spectra of N₂H₄ without (a) and with (b) the discharge, and, in addition, illustrates the effect of adding increasing amounts of HCl to the discharge products (c, d and e). Fig. 27 and 28 illustrate the analogous procedure for the deuterated system, except here the effect of DCI was monitored using only the first bands of ND₃ and N₂D₂ in Fig. 23. In both cases, it has been found that the gas phase reactions of HCl(DCl) with NH₃(ND₃) is instantaneous, giving a white deposit of NH₄Cl(NH₄Cl) on the walls, whereas the reaction of HCl(DCl) with N₂H₂(N₂D₂) is very slow. We have done further experiments on the reaction of HCl with pure N₂H₂, generated by the 2nd method, and have
FIGURE 26

(e) EXCESS HCl

(d) MORE HCl

(c) HCl ADDED

(b) DISCHARGE IN $N_2H_4$

(a) $N_2H_4$

IONIZATION POTENTIAL (eV)

INTENSITY (ARBITRARY)
(b) DISCHARGE IN $N_2D_4$

- $N_2D_2$
- $N_2D_2$
- $N_2/537\AA$
- $N_2$
- $N_2$
- $ND_3$

(a) $N_2D_4$

- $D_2O$

IONIZATION POTENTIAL (eV)

FIGURE 27
(a) NO DCI

(b) DCI ADDED

(d) EXCESS DCI

(c) MORE DCI

IONIZATION POTENTIAL (eV)

FIGURE 28
observed the same behavior. By using the right amount of HCl(DCl), the resulting spectrum of $N_2H_2(\bar{N}_2O_2)$ may then be obtained free from $NH_3(\overline{\nu}_3)$ interference (Fig. 26d and Fig. 28c), and, in some cases, contains additional bands due to HCl(DCl) (Fig. 26e and 28d), which prove useful for calibration purposes.

The experimentally determined IP's and vibrational frequencies are collected in Table 6, where the vibrational frequencies of the ground state molecules are also listed for comparison. The $NH_3$-free spectrum of $N_2H_2$ obtained by the second method, which because of its favorable $N_2H_2/H_2$ ratio gives a better presentation of the $N_2H_2$ bands, is shown in Fig. 29.

$HN=NH$ The PE spectrum of $N_2H_2$ (Fig. 29) exhibits four distinguishable bands, with extensive vibrational structure on all of them. The first band (Fig. 30) has an adiabatic IP of 9.59 eV, and a vertical IP of 10.02 eV. This compares favorably with the only previously determined value of $9.85 \pm 0.1$ eV from mass spectrometry\textsuperscript{178}. The band envelope extends over ca. 1.3 eV, with at least 12 components, the vertical transition occurring at $\nu' = 3$. The vibrational interval between the 0 and 1 vibrational quanta is 1180 cm\textsuperscript{-1}, however, this tends to decrease towards high vibrational quanta, the value averaged over 0 to 9 being 1050 cm\textsuperscript{-1}. There is also the suggestion of another series, possibly starting at $\sim 1800$ cm\textsuperscript{-1} above the $\nu' = 0$ peak between the $\nu' = 1$ and 2 vibrational components of the primary series. Here the vibrational spacing between members is a constant 1180 cm\textsuperscript{-1}. 
<table>
<thead>
<tr>
<th>Ionic state</th>
<th>$N_2H_2$</th>
<th>$N_2D_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vertical IP (adiabatic) (eV)</td>
<td>$\nu$(cm$^{-1}$)</td>
</tr>
<tr>
<td>$X^2A_g$</td>
<td>10.02 (9.59)</td>
<td>1180</td>
</tr>
<tr>
<td>$B^2B_u$</td>
<td>15.03 (14.71)</td>
<td>1170</td>
</tr>
<tr>
<td>$C^2A_g$</td>
<td>16.9 (16.19)</td>
<td>940</td>
</tr>
</tbody>
</table>

* from ref. 182.
IONIZATION POTENTIAL (eV)

FIGURE 29
Towards higher vibrational quantum numbers the two series appear to merge, making precise measurements difficult.

The second band (Fig. 30) has an adiabatic IP of 14.10 eV, and a vertical IP of 14.39 eV. Here the band envelope contains at least 7 members spreading over about 0.8 eV, with a fairly even vibrational spacing of 1110 cm$^{-1}$. The vertical transition occurs at $v' = 2$.

The third band (Fig. 30) is overlapped by the second band, but the adiabatic and vertical IP's can be confidently assigned at 14.71 eV and 15.03 eV, respectively. Here the band shows at least five discernible peaks with the vertical transition occurring at $v' = 2$.

The first five vibrational components of the fourth band are clearly distinguishable, but the higher energy side of the band is concealed by the intense second band of $N_2$ (Fig. 30). Judging from the intensity under the latter, we expect the progression of the fourth band to be quite extensive, spreading over about 1.5 eV, and estimate the vertical IP at 15.9 eV. The adiabatic IP can be accurately assigned at 16.19 eV and the average vibrational spacing over the first five components is 940 cm$^{-1}$.

The PE spectrum of $N_2D_2$ (Fig. 27) is in many respects similar to that of $N_2H_2$. Subtle differences induced by deuteration, however, enable us to be more confident about our assignments (see below).

The first band (Fig. 31) has an adiabatic IP of
9.61 eV, and a vertical IP of 10.10 eV. In this case, the vertical transition occurs at \( v' = 4 \), with the 0-0 transition having a much lower probability. The first vibrational spacing is 1020 cm\(^{-1}\), this decreasing to an average of 980 cm\(^{-1}\) over the first 4 intervals, and to 880 cm\(^{-1}\) over the first 9 intervals. Again there is the suggestion of another vibrational series, but in view of the experimental difficulties, and narrower vibrational spacing it is impossible to be specific.

The second band (Fig. 31) has an adiabatic IP of 14.11 eV and a vertical IP of 14.39 eV. This occurs at \( v' = 2 \), the band envelope spreading over 8 distinguishable components. The vibrational spacing is fairly constant at 1110 cm\(^{-1}\), and so in all respects it is identical to the second band of \( \text{N}_2\text{H}_2 \).

The third band (Fig. 31) again overlaps with the second band, but we are confident in assigning the adiabatic IP to 14.69 eV. (The agreement with the analogous value of \( \text{N}_2\text{H}_2 \) tends to support the correct assignment of the adiabatic transition). The vertical transition poses more of a problem, due to overlapping with the 537 Å shadow of the second band of \( \text{N}_2 \). However, the general shape of the FC envelope, which extends over at least five vibrational components, suggests the vertical transition to occur around \( v' = 3 + 1 \), i.e. at 15.17\( \pm \)0.12 eV. This assignment is consistent with the corresponding vertical IP of \( \text{N}_2\text{H}_2 \), (which
occurs at v' = 2) since the vibrational spacing for N₂D₂, which averages 960 cm⁻¹ (over the first 4 intervals), is 210 cm⁻¹ smaller than that for N₂H₂, and thus a more extensive vibrational progression is expected for N₂D₂.

The fourth band is completely concealed by D₂ and the second band of N₂ (Fig. 27b), and thus cannot be observed.

4.4.4 Discussion

The assignments for the PE spectra are assisted by the analysis of the vibrational structure, the effect of deuteration, comparison with other azo compounds and with MO calculations.

By comparison with other azo compounds¹⁹³⁻¹⁹⁵, the first band can be assigned to the n⁺(a_g) orbital (N₂H₂ assumes C₂h symmetry), i.e. the symmetric combination of N lone pairs. This assignment is corroborated by the vibrational structure which starts at 1180 cm⁻¹ (for N₂H₂) and which steadily decreases to ca. 980 cm⁻¹ around the 10th vibrational quantum number. For the neutral molecule ν₂ (δNNH) is 1583 cm⁻¹¹⁸², and if this is the mode excited we observe a decrease of at least 400 cm⁻¹. This is to be anticipated if there is a large opening of the NNH angle, which is expected if an electron from the n⁺ orbital is removed. The PE spectrum of the deuterated species confirms this assignment since here the vibrational structure on the first band decreases from 1020 cm⁻¹ to ca. 800 cm⁻¹ (at the 9th
vibrational quantum number). This compares with the value of 1215 cm\(^{-1}\) for \(\nu_2\) in the neutral molecule \(\text{N}_2\text{D}_2\). The first components of both \(\text{N}_2\text{H}_2\) and \(\text{N}_2\text{D}_2\) are within the limits of the zero point energy giving us confidence regarding the value of the adiabatic IP.

The other vibrational structure with an average spacing of ca. 1800 cm\(^{-1}\), which if genuine, may be assigned to the symmetric N-N stretch \((\nu_3)\), which is 1529 cm\(^{-1}\) in the neutral molecule.

The relative ordering of the bands corresponding to the \(n_-(b_u)\) orbital, i.e. the antisymmetric combination of the N lone pairs, and the N-N \(\pi (a_u)\) orbital cannot be unequivocally assigned on the basis of the vibrational structure in \(\text{N}_2\text{H}_2\) alone. Thus, both the second and third bands have vibrational structure in the range 1100 to 1200 cm\(^{-1}\), and in the neutral molecule \(\nu_2\) and \(\nu_3\) are 1583 and 1529 cm\(^{-1}\) respectively. However, upon deuteration the vibrational structure on the second band remains exactly the same (1110 cm\(^{-1}\)), whereas that on the third band drops to 960 cm\(^{-1}\). Thus we can confidently assign the second band to the \(\pi\) ionization and the third band to the \(n_-\) orbital.

The fourth band can be assigned to the strongly bonding N-N \(\sigma (a_g)\) orbital. This assignment is in line with the large decrease, i.e. ca. 600 cm\(^{-1}\), in the \(\nu_3\) (N-N stretch) frequency of the ion.

The above assignments for the bands and vibrational structure are wholly supported by ab initio calculations\(^{62,186-189}\).
In addition, these calculations consistently predicted that only four IP's are below 21.22 eV, thus suggesting that the HeI PE spectrum of \( \text{H}_2\text{H}_2 \) presented here is complete.

As the prototype of the azo compounds, \( \text{H}_2\text{H}_2 \) has by far the largest \( n_+ - n_- \) separation (\( \Delta E = 5.1 \text{ eV} \)) yet observed for adjacent nitrogen atoms. To date the largest observed value is to be found in 3,3 dimethyl diazirine (\( \Delta E = 3.55 \text{ eV} \)). The large splitting in \( \text{H}_2\text{H}_2 \) may be attributed to the dual facts that for this molecule the nitrogen 'lone' pairs have the largest contribution in \( n_+ \) and \( n_- \) orbitals. This, coupled with the 180° dihedral angle gives maximum overlap and thus interaction for the N lone pairs.

It is of interest to compare the PE spectrum of difluorodiazene, \( \text{H}_2\text{F}_2 \), with that of \( \text{H}_2\text{H}_2 \). Due to the uncertainty in the higher IP's, only the \( n_+ \) and \( \pi \) levels in \( \text{H}_2\text{F}_2 \) have been assigned, and are at 13.4 and 14.1 eV respectively. These compare with the \( n_+ \) and \( \pi \) ionizations of \( \text{H}_2\text{H}_2 \) at 10.0 and 14.4 eV respectively, indicating a positive perfluoro shift of 3.4 eV on the \( n_+ \) ionization and a negative perfluoro shift of 0.3 eV on the \( \pi \) level. Such a large positive shift for the \( n_+ \) level is indicative of the large contribution of the F atoms to this orbital in \( \text{H}_2\text{F}_2 \), and parallels the value of +3.6 eV obtained from the calculation. The negative value for the \( \pi \) ionization is unusual, the only other negative value for such an ionization being observed on the \( \text{C}_2\text{H}_2 \) and \( \text{C}_2\text{F}_2 \) system (-0.14 eV). It is most
probable that this effect arises from a stabilization of the ionic state by delocalization over the F atoms. The overall result is thus in accord with the conclusions of the perfluoro effect, i.e. that the \( \pi \) ionization shift is small in comparison to the \( \sigma \) ionization shift. The Franck-Condon envelopes for the \( \pi \) ionization in \( \text{N}_2\text{F}_2 \) and \( \text{N}_2\text{H}_2 \) are similar, again illustrating the relatively small effect of the F atoms on the \( \pi \) ionization.

In comparing the vacuum ultraviolet (1700\( \text{Å} \)) absorption bands\(^{181}\) of \( \text{N}_2\text{H}_2 \) and \( \text{N}_2\text{D}_2 \) with their respective first PE bands, we notice a number of similarities, which tend to suggest that the absorption band is probably a Rydberg transition leading to the first IP of the molecule. First, both the absorption and PE bands show an extensive progression in \( v_2 (\delta\text{NNH}) \). Significantly, the vibrational frequencies are quite similar in the two cases, being 1192 and 1180 cm\(^{-1} \) (0-1 spacing) for the absorption and PE bands of \( \text{N}_2\text{H}_2 \), and 955 and 1020 cm\(^{-1} \) for the corresponding deuterated cases. Secondly, the single quantum excitation in N-N stretching mode in the absorption band also appears in the PE band and has similar frequencies, i.e. 1374 cm\(^{-1} \) and \( \approx 1300 \) cm\(^{-1} \) for the absorption and ionization respectively. Thirdly, the FC envelopes of the two bands are similar. Although the vertical transitions in the absorption bands\(^{181}\) of \( \text{N}_2\text{H}_2 \) and \( \text{N}_2\text{D}_2 \) appear to occur one quantum number lower than that in their respective PE bands, this difference
may not be certain in view of the overlap of the absorption band by the strong bands of \( \text{NH}_3 \), which inevitably causes difficulty in assigning the vertical transition. Furthermore, using the experimental FCF, we have estimated (section 2.2.3.c) an increase of 20° in the N-N-H angle, which, quite significantly, is also the angle increase estimated for the excited state \(^{181}\). Treating the absorption band as a Rydberg transition and using the experimentally determined IP value, the quantum defect is calculated to be 0.62 for the Rydberg state with a principal quantum number \( N=3 \). This value for the quantum defect is in the expected region \(^{196}\) for \( \text{N} 3\text{P} \) Rydberg orbitals, and thus tends to support our assertion.

Recently, the near ultraviolet absorption spectra (3000-4300 Å, \( \pi^*\rightarrow n_+ \) transition) of the \( \text{N}_2\text{H}_2 \) and \( \text{N}_2\text{D}_2 \) have been studied in great detail by Back et al.\(^{185}\). However, they could not rule out the possibility that a small fraction of the cis isomer, with an extinction coefficient 10 or 20 times that of the trans isomer, is responsible for the spectra. In the light of our results, it is of interest to investigate this possibility further. Both the absorption and the first ionization involve the highest occupied \( n_+ \) orbital, and consist of an extensive vibrational progression in \( v_2 \). We note in particular, however, that the FC envelope is more extensive in the absorption case, in that for \( \text{N}_2\text{H}_2 \) the vertical transition in absorption occurs at \( v'=6 \) compared to \( v'=3 \) in ionization, and for \( \text{N}_2\text{D}_2 \) they are respectively at \( v'=3 \) and 4.
Moreover, the increase in the N-N-H angle is estimated to be \(25^\circ\) in the excited state whereas it is only \(20^\circ\) in the ground ionic state. These trends in vibrational progression and angle increase appear to be in conflict with our expectation, since the opposite is to be anticipated in view of the larger perturbation caused by the ionization process, and the \(\pi^*\) orbital (involved in the absorption) has hardly any influence on the N-N-H angle. Therefore, on this basis we would not rule out the possibility of the cis isomer playing a role in the absorption spectrum.

From the PE spectra, it seems pertinent to make a comment regarding the possibility of the ground state of diazene being a triplet as suggested by Trombetti based upon the analysis of the rotational structure in the 1700 Å absorption band. The simplicity of the PE spectrum of diazene and the fact that the spectrum can be convincingly assigned on the basis of a singlet ground state strongly argues against a triplet ground state.

4.5 Trans-methyldiazene (\(\text{CH}_3\text{N}=\text{NH}\))

The monomethyl substituted derivative of \(\text{N}_2\text{H}_2\), \(\text{CH}_3\text{NNH}\), has also attracted a great deal of attention recently. Despite its relative stability compared to \(\text{N}_2\text{H}_2\), the study and understanding of \(\text{CH}_3\text{NNH}\) is far less complete than that of the former. In the following, preliminary results on the PE spectrum of this species are presented.
CH$_3$NNH was prepared in a weak microwave discharge in the equilibrium vapor of methylhydrazine at room temperature. Undischarged methylhydrazine and involatile products were trapped at -78°C leaving only CH$_3$NNH/HH$_3$/H$_2$/CH$_4$ in the gas phase. Elimination of NH$_3$ was achieved by trapping these gas phase products at -196°C, and holding the products at -120°C (methylcyclohexane slush bath). Pumping the products through the ionization chamber, we observed the spectra of NH$_3$ and CH$_4$, and traces of C$_2$H$_6$, until finally the spectrum of CH$_3$NNH was observed, free of any other species.

The efficiency of the discharge in selectively producing CH$_3$NNH was monitored by observing the yellow color$^{200}$ of CH$_3$NNH in the -196°C trap. In this respect, we also have confirmation of the production of the desired species. The resemblance of the PE spectrum of CH$_3$NNH (Fig. 32a) with that of CH$_3$NNCH$_3$ (Fig. 32b) and N$_2$H$_2$ (Fig. 29, neglecting the vibrational fine structure of the individual bands) provides further evidence for the correct spectrum. The identification of the spectrum is, moreover, substantiated by the observation of H$_2$ bands in the subsequent spectrum of CH$_3$NNH (Fig. 32a), which can only result from the decomposition of this species. An additional proof of its positive identification by preparing the species from an alternative route$^{200}$ is presently in progress.

The PE spectrum of CH$_3$NNH (Fig. 32a) consists of five distinct, featureless bands. The absence of vibrational structure on any of them is understandable in view of the low symmetry (C$_s$) of the molecule. The intensity and the
shape of the second band strongly suggest that it consists of two overlapping IP's, which is further supported by comparison with the spectra of \( \text{N}_2\text{H}_2 \) and \( \text{CH}_3\text{NNCH}_3 \) (see below). The experimental results are gathered in Table 7.

The assignment of the spectrum of \( \text{CH}_3\text{NNNH} \) is fairly straightforward by comparison with the closely related molecules \( \text{N}_2\text{H}_2 \) and \( \text{CH}_3\text{NNCH}_3 \). Consideration of the effect of introducing a \( \text{CH}_3 \) group into \( \text{N}_2\text{H}_2 \) leads us to expect that the individual bands of \( \text{CH}_3\text{NNNH} \) would be shifted to lower IP value compared to the corresponding bands of \( \text{N}_2\text{H}_2 \). This trend is expected to continue on going from \( \text{CH}_3\text{NNNH} \) to \( \text{CH}_3\text{NNCH}_3 \). This is, indeed, what is observed (see Fig. 32 and Fig. 29), if the 2\(^{\text{nd}}\) band of \( \text{CH}_3\text{NNH} \) is due to two IP's. Therefore, the same relative ordering \( n_+, \pi_{\text{N-H}}^+, n_- \) and \( \sigma_{\text{N-H}}^+ \) can be assigned to \( \text{CH}_3\text{NNNH} \) as in the case of \( \text{N}_2\text{H}_2 \) (section 4.4.4) and \( \text{CH}_3\text{NNCH}_3 \). The two highest IP's are tentatively assigned on the basis of CNDO/2 and INDO calculations (Table 7).
TABLE 7  PES and Theoretical Ionization Potentials (in eV) of CH$_3$NNH

<table>
<thead>
<tr>
<th>Ionic state</th>
<th>PES Vertical IP (adiabatic)</th>
<th>Theoretical</th>
<th>Orbital</th>
<th>CNDO/2 *</th>
<th>INDO *</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2A'$</td>
<td>9.57 (3.8)</td>
<td>7a$^\dagger$(n$_+$)</td>
<td>9.3</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>$^2A''$</td>
<td>12.9 (12.05)</td>
<td>2a$^\dagger$(\Pi$_{N=H}$)</td>
<td>11.4</td>
<td>11.3</td>
<td></td>
</tr>
<tr>
<td>$^2A'$</td>
<td>13.4</td>
<td>6a$^\dagger$(n$_-$)</td>
<td>16.3</td>
<td>14.8</td>
<td></td>
</tr>
<tr>
<td>$^2A'$</td>
<td>14.74 (14.4)</td>
<td>5a$^\dagger$(\sigma$_{H-N}$)</td>
<td>12.9</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td>$^2A''$</td>
<td>15.58 (15.2)</td>
<td>1a$^\dagger$(\Pi$_{C=H}$)</td>
<td>18.2</td>
<td>18.0</td>
<td></td>
</tr>
<tr>
<td>$^2A'$</td>
<td>16.72 (16.3)</td>
<td>4a$^\dagger$</td>
<td>20.3</td>
<td>19.3</td>
<td></td>
</tr>
</tbody>
</table>

* with 4 eV adjustment.
CHAPTER FIVE

PHOTOELECTRON SPECTROSCOPY OF SOME REACTIVE MOLECULES

5.1 Methiophosphide (HCP)

5.1.1 Introduction

The phosphorous analog of hydrogen cyanide (HCN), methiophosphide (HCP), is an unusual and interesting molecule in that it is the only isolated compound with a phosphorous atom bonded to only one neighboring atom, presumably through a carbon-to-phosphorous triple bond. Because of this unusual feature and its similarity to HCN, a photoelectron spectroscopic study of HCP was carried out. In addition, the results threw light on the as yet unresolved first PE band of HCN\(^{205}\).

5.1.2 Experimental

HCP was first prepared in 1961 by Gier\(^{206}\) and our method of synthesis followed his, in which phosphine was passed through a low intensity (70-80 amperes, 20 volts)
Carbon Arc Reactor

MATERIALS

STAINLESS STEEL (304)
OTHERS UNSPECIFIED - BRASS, COPPER

FIGURE 33
rotating arc struck between a pair of specially constructed carbon electrodes (Fig. 33). About four parts of acetylene to one of HCP$_{206}$ were formed in the reaction, but because of the very reactive$^{206}$ and unstable (stable for a few hours at room temperature$^{207}$) character of HCP, no attempt was made to separate the two compounds.

The PE spectrum of HCP was recorded immediately after its synthesis and calibrated against the known ionization potentials (IP's) of xenon and acetylene. The sample was kept at -160°C (isopentene slush bath) in the Kel-F container (section 3.3.4.b) and the pressure was further controlled by the Kel-F valve.

5.1.3 Results And Discussion

Despite the presence of acetylene and traces of phosphine and ethylene it was possible to determine the first two of the three expected IP's of HCP under high resolution (Fig. 34). The third IP evaded detection, presumably because of its weak cross section as is the case for the corresponding IP of HCN, and we suspect it may very well be buried underneath the 2nd or 3rd bands from acetylene. The experimental results summarized in Table 8 compare favorably with a recent extensive ab initio MO calculation on HCP$_{208}$. This agreement together with the experimental observation of the vibrational fine structure in each
# TABLE 8 PES and Theoretical Data of HCP

<table>
<thead>
<tr>
<th>Orbital assignment* and characteristics</th>
<th>Ionization potentials (eV)</th>
<th>Vibrational frequencies (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MO calculation*</td>
<td>PES</td>
</tr>
<tr>
<td>1π (C-P bonding only)</td>
<td>10.0</td>
<td>10.793±0.005</td>
</tr>
<tr>
<td>3σ (lone pair electrons on P atom)</td>
<td>12.6</td>
<td>12.855±0.005</td>
</tr>
<tr>
<td>2σ (mainly C-H bonding)</td>
<td>20.0</td>
<td>--</td>
</tr>
</tbody>
</table>

* from Ref. 208.
band shows quite conclusively that the first and second IP's are from the π and σ MO's respectively, and the orbital configuration of HCP for the valence shell is \((l\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4\). The first band (Fig. 34) with a vibrational spacing of 1110 cm\(^{-1}\) (a decrease from 1276 cm\(^{-1}\) in the ground molecular state) comes from the C-P bonding π-orbital as predicted by the calculation\(^{208}\). The second band (Fig. 2) is typical of a non-bonding orbital, because of its sharpness and a vibrational frequency little changed from the neutral molecule.

5.2 \(\text{CSe}_2, \text{OCSe And SCSe}\)

5.2.1 Introduction

There are six triatomic linear molecules containing carbon and oxygen, sulfur or selenium, OCO, OCS, SCS, OCSe, SCSe and SeCSe. The first three have been studied extensively both by optical\(^{209}\) and photoelectron\(^{3,172}\) spectroscopy; however, the spectroscopic data for the other three is very limited. The toxicity, unpleasant odors (even in very low concentrations), other adverse physiological effects, instability and the difficulty of obtaining them in pure form make these molecules unappealing to spectroscopists. In this section, the PE spectra of these selenium compounds are presented and discussed, and the spectra of \(\text{CO}_2, \text{OCS}\)
and CS$_2$ have been included for the sake of comparison and completeness.

PES has in recent years stimulated a growing interest in the quantitative formulation and application of the Franck-Condon principle to polyatomic molecules$^{210}$. The major motive behind these studies has been to determine the geometry of ionized molecules from experimentally determined relative vibrational transition probabilities. The general approach in all these studies has been to assume a constant electronic transition moment, thus reducing the problem to an evaluation of vibrational overlap integrals, i.e. the Franck-Condon overlaps, and to use the harmonic oscillator approximation to simplify the integration. Although the theoretical Franck-Condon factor (FCF) may not reproduce the experimental one quantitatively, qualitative agreement is always obtained$^{210}$. From past experience, it is reasonable to expect that the best geometry will give a set of FCF's in best agreement with experiment. We have checked this expectation by determining the geometry of the ionic states of the molecules studied here employing the procedure outlined in section 2.2.3.c, and comparing them, where possible, with experimental data, in the hope that a systematic and reliable way of determining ionic geometry can be established. An attractive feature of these structurally and chemically similar compounds is that several "analogous" series are available for study.
5.2.2 Experimental

CO₂, OCS and CS₂ were obtained commercially (Matheson) and were used without further purification. CSe₂ was prepared by passing methylene chloride vapor over molten selenium at about 500°C. Selenium was removed by steam distillation and the majority of methylene chloride by simple distillation. The residue from simple distillation was subjected to repeated processes of freezing (-78°, dry ice-acetone bath), thawing and pumping at -78°C. The spectrum of CSe₂ was finally recorded when the PE bands of methylene chloride were no longer in evidence. OCSe was obtained in low yield by passing carbon monoxide gas over molten selenium at about 500°C. The reaction vessels were kept scrupulously dry. Traces of carbon monoxide were removed by pumping. SCSe was synthesized by mixing CS₂ vapor with selenium vapor at about 500°C and heating the mixture at about 750°C. Selenium was removed by simple distillation and the bulk of CS₂ by fractional distillation. The SCSe enriched solution of CS₂ was then subject to trap (-78°C) to trap (-195°C) distillation. The last trace of CS₂ was pumped away at -78°C.

The IR spectra of the prepared selenium compounds agreed very well with previously reported work and showed little impurity. All the selenium compounds were found to decompose readily in contact with metal, OCSe being the most serious. The deposition of selenium inside the ionization
chamber caused severe deterioration in the instrumental resolution. To alleviate this problem, two procedures were taken; (1) The ionization chamber was differentially pumped to shorten the time of contact between the sample and the metallic surfaces, (2) A glass sample inlet system (section 3.3.4.b) was adopted (for OCSe), because the CO formed by decomposition interfered strongly with the PE spectrum of OCSe. The pressure of the sample was controlled by an appropriate slush bath (isopentane for OCSe) and a teflon stop cock. With these precautions taken, it was still necessary to clean the vacuum chamber frequently, especially the ionization chamber. Procedure (2) was not adopted for CSe₂ and SCSe, where the decomposition products did not interfere with the spectra of the parent compounds.

The spectra were recorded with a resolution between 20-30 meV (measured by FWHM of the argon doublet) and calibrated against appropriate noble gases. The ionization potentials (IP's) were accurate to 0.01 eV and vibrational frequencies to 30 cm⁻¹, unless specified otherwise.

5.2.3 Results

The PE spectrum of each compound is shown in Fig. 35. The experimental results are tabulated in Table 9, where the vibrational frequency for the ground state of each neutral molecule is also included for comparison.
FIGURE 35

a) CO$_2$

b) CS$_2$

c) CSe$_2$

d) OCS

e) OCSe

f) SCSe

COUNTS/SEC (ARBITRARY UNITS)

IONIZATION POTENTIAL (eV)
<table>
<thead>
<tr>
<th>Molecule</th>
<th>Electronic state</th>
<th>Adiabatic IP's (^a) (eV)</th>
<th>Vibrational frequencies (^b) (cm(^{-1}))</th>
<th>spin-orbit splitting (^d) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CO}_2)</td>
<td>(\chi^1\Sigma^+)</td>
<td>--</td>
<td>1383</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>(\chi^2\Pi_g)</td>
<td>13.80</td>
<td>667</td>
<td>2349</td>
</tr>
<tr>
<td></td>
<td>(\chi^2\Pi_u)</td>
<td>17.34 (17.60)</td>
<td>1440</td>
<td>0.020</td>
</tr>
<tr>
<td>(\text{CO}_2^+)</td>
<td>(\chi^2\Pi_g)</td>
<td>18.08</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>(\chi^2\Pi_u)</td>
<td>19.39</td>
<td>1470</td>
<td>--</td>
</tr>
<tr>
<td>(\text{CS}_2)</td>
<td>(\chi^1\Sigma^+)</td>
<td>--</td>
<td>658</td>
<td>397</td>
</tr>
<tr>
<td></td>
<td>(\chi^2\Pi_g)</td>
<td>10.06</td>
<td>397</td>
<td>313</td>
</tr>
<tr>
<td></td>
<td>(\chi^2\Pi_u)</td>
<td>12.67 (12.81)</td>
<td>313</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>(\chi^2\Sigma_g^+)</td>
<td>16.18</td>
<td>313</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>(\chi^2\Sigma_u^+)</td>
<td>16.70 (17.08)</td>
<td>313</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>CI state</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>(\text{CSe}_2)</td>
<td>(\chi^1\Sigma^+)</td>
<td>--</td>
<td>368</td>
<td>1303</td>
</tr>
<tr>
<td></td>
<td>(\chi^2\Pi_g)</td>
<td>9.27</td>
<td>368</td>
<td>1303</td>
</tr>
<tr>
<td></td>
<td>(\chi^2\Pi_u)</td>
<td>11.49 (11.69)</td>
<td>368</td>
<td>1303</td>
</tr>
<tr>
<td></td>
<td>(\chi^2\Sigma_g^+)</td>
<td>15.90</td>
<td>368</td>
<td>1303</td>
</tr>
</tbody>
</table>
TABLE 9 (cont'd) PES Data for CO₂, CS₂, CSe₂, OCS, OCSe and SCSe

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Electronic state</th>
<th>Adiabatic IP's (eV)</th>
<th>Vibrational frequencies (cm⁻¹)</th>
<th>spin-orbit splitting (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>v₁</td>
<td>v₂</td>
</tr>
<tr>
<td>OCS</td>
<td>X¹Σ⁺</td>
<td>--</td>
<td>2062 b)</td>
<td>520 b)</td>
</tr>
<tr>
<td></td>
<td>X²Π</td>
<td>11.18</td>
<td>2030</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>A²Π</td>
<td>15.09</td>
<td>1990</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>B²Σ⁺</td>
<td>16.05</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>C²Σ⁺</td>
<td>17.96</td>
<td>2150</td>
<td>--</td>
</tr>
<tr>
<td>OCSe</td>
<td>X¹Σ⁺</td>
<td>--</td>
<td>2021 c)</td>
<td>466 c)</td>
</tr>
<tr>
<td></td>
<td>X²Π</td>
<td>10.36(10.43)</td>
<td>2100±50</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>A²Π</td>
<td>14.58(14.73)</td>
<td>2000±100</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>B²Σ⁺</td>
<td>15.75</td>
<td>1930±100</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>C²Σ⁺</td>
<td>17.90</td>
<td>2100</td>
<td>--</td>
</tr>
<tr>
<td>OCSe⁺</td>
<td>X¹Σ⁺</td>
<td>--</td>
<td>1435 c)</td>
<td>355 c)</td>
</tr>
<tr>
<td></td>
<td>X²Π</td>
<td>9.58</td>
<td>1220±50</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>A²Π</td>
<td>12.13(12.35)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>B²Σ⁺</td>
<td>14.07</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>C²Σ⁺</td>
<td>16.06</td>
<td>930±50</td>
<td>--</td>
</tr>
</tbody>
</table>
TABLE 9 (cont'd) PES Data for CO$_2$, CS$_2$, CSe$_2$, OCS, OCSe and SCSe

a) values in parentheses are vertical IP's
b) from ref. 209
c) from ref. 214
d) experimental error ± 0.004 eV
Our results and interpretation of the PE spectra for these compounds are in complete agreement with the previous studies (see discussion below), accordingly no further discussion will be given here.

The spectrum of CSe$_2$ (Fig. 35c) exhibits four distinguishable bands, and vibrational structure is resolved on two of them. The adiabatic IP of the first band is 9.27 eV. This band consists of two equally intense peaks which are the doublet components $^2 \Pi_{3/2}, ^2 \Pi_{1/2}$, with a spin-orbit splitting of 0.265 eV. The second band (Fig. 36a) shows an extensive, simple vibrational progression in $v_1$. It spreads over approximately 0.5 eV and consists of at least 12 components with an average spacing 320 cm$^{-1}$. The adiabatic and vertical IP's are 11.49 and 11.69 eV respectively. The third band (Fig. 36b) has an identical adiabatic and vertical IP at 13.63 eV. It shows two levels of vibrational excitation in $v_1$ with a spacing of 310 cm$^{-1}$. The fourth band is a single peak with an IP at 15.90 eV.

Four bands are distinguishable in the spectrum (Fig. 35e), and vibrational fine structure is seen on all four. The second and third bands overlap (as in OCS) and
Figure 36

Ionization Potential (eV)

Counts/sec (Arbitrary Units)

$A^2\Pi_u$

$B^2\Sigma_u^+$
the overall form of the spectrum is very similar to that of OCS, with the bands of the latter being slightly higher in energy.

Considerable overlap occurs in the first band (Fig. 37a). The band, however, can be satisfactorily analyzed if the first and fourth peaks are treated respectively as the origins of the doublet components $^2\Pi_{3/2}$, $^2\Pi_{1/2}$. This assignment is strongly supported by the experimental fact that the appearance of the first three peaks is reflected in the next three, except for a difference in intensity (see below). This gives a $^2\Pi_{3/2} - ^2\Pi_{1/2}$ splitting of 0.207 eV and the adiabatic and vertical IP's at 10.36 and 10.43 eV respectively. A vibrational progression in $v_3$ with an average spacing of 500 cm$^{-1}$ is clearly discernible in each of the doublet components. Judging from the intensity distribution of the progression, at least four levels of excitation are expected for $v_3$. This means the (003) and (004) components of the $^2\Pi_{3/2}$ state are buried underneath the $^2\Pi_{1/2}$ band. A single level excitation in $v_1$ is also observed with an average spacing of 2100 cm$^{-1}$. The progression (10$n_3$) of the $^2\Pi_{1/2}$ state can be distinguished, with $n_3 = 0,1,2,$ and 3, while the corresponding progression of the $^2\Pi_{3/2}$ state is completely overlapped by the (00$n_3$) progression of the former state. This explains the greater intensity of the $^2\Pi_{1/2}$ band.
FIGURE 37

- $a) X^2\Pi$
- $b) A^2\Pi, B^2\Sigma^+$
- $c) C^2\Sigma^+$

IONIZATION POTENTIAL (eV)
The second band (Fig. 37b), with adiabatic IP at 14.58 eV consists of at least 15 peaks spreading over about 1 eV. The regular spacing of 590 cm\(^{-1}\) suggests a progression in \(v_3\), yet the complexity and the irregular intensity distribution of the band tend to suggest more than one vibrational progression. As in OCS, the additional excitation of \(v_1\) is most likely. Judging from the intensity variation profile of the band, a spacing of ca. 2000 cm\(^{-1}\) is assigned to \(v_1\). The third peak at 14.73 eV is then taken as the vertical transition. This uncertainty arises because of the overlap with the much more intense third band. The third band (Fig. 37b, adiabatic IP 15.75 eV) is a very intense sharp peak with perhaps another peak at 1930 cm\(^{-1}\) to higher energy, assigned to \(v_1\) by comparison with the ground-state frequency. The fourth band (Fig. 37c, adiabatic IP 17.90 eV) shows two ionic frequencies to be involved, as in OCS. They are assigned to \(v_1\) and \(v_3\) respectively, by comparison with the molecular ground-state frequencies.

SCSe

Four bands can be distinguished in the spectrum (Fig. 35f), each showing vibrational fine structure.

The adiabatic IP for the first band is 9.58 eV (Fig. 38a). The peaks occur in pairs indicating the splitting of the state into doublet components \(2\Pi_3^2, 2\Pi_1^2\) with a spin-orbit splitting of 0.135 eV. Analysis of the vibrational fine structure indicates single quantum level excitation of
FIGURE 38

a) $X^2\Pi$

b) $A^2\Pi$

c) $B^2\Sigma^+$

d) $C^2\Sigma^+$

IONIZATION POTENTIAL (eV)

COUNTS/SEC (ARBITRARY UNITS)
two ionic frequencies to be involved. One is $v_3$, and the other $v_1$. The (100) peak of the $2\Pi_{3/2}$ state overlaps with the (000) peak of the $2\Pi_{3/2}$ state. The second band (Fig. 38b, adiabatic IP 12.13 eV, vertical IP 12.35 eV) consists of a long series of peaks, spreading over approximately 0.6 eV. At least ten peaks are resolved with an average spacing of 440 cm$^{-1}$, which is assigned to $v_3$. The third band (Fig. 38c, adiabatic IP 14.07 eV) consists of a single quantum of excitation in $v_3$. The fourth band (Fig. 38d, adiabatic IP 16.06 eV) indicates a single quantum of excitation in both $v_1$ and $v_3$.

5.2.4 Discussion

Assignment Of The PE Spectra

The assignment of the PE spectra of the selenium compounds studied here can easily be accomplished by a simple correlation with the known ionic states of CO$_2$, OCS and CS$_2$\textsuperscript{3,172}. The identification of vibrational fine structure of each band can be facilitated by comparison with the molecular ground-state frequencies and by considering the following selection rules for vibrational excitation (section 2.2.4.b); (1) Totally symmetric vibrations may assume any quantum number in the ionic state; (2) Vibrations antisymmetric with a symmetry species can only assume zero or even quantum number.

An examination of Fig. 35 shows the general resemblance of all the PE spectra. Typically, the second band of
each molecule shows an extensive vibrational progression indicating a considerable change in geometry from the molecule to ion and the ionized electron must therefore have come from a strongly bonding or antibonding MO. The other three bands show less or little vibrational fine structure, indicating little change in geometry and the involvement of a more or less nonbonding electron in each case. In addition, the first PE band of each molecule shows a resolvable spin-orbit splitting (except CO$_2$). Considering these resemblances and the chemical similarity between the compounds, we conclude that the order of ionic states is the same throughout the series.

A correlation diagram of ionic states is shown in Fig. 39, and it shows several interesting trends. The energy of each ionic state is lowered if one end atom is substituted by a heavier one. The effect of substitution of S by Se is much smaller than that of O by S or Se. The latter substitutions result in an energy lowering greater than 1 eV, while the former produce far less than 1 eV. This reflects a well established fact that the resemblance between two successive elements in a periodic group is closer as one proceeds down the group. The trend in the magnitude of spin-orbit splitting $A$ of the ground ionic state is as expected except perhaps where that of OCS$\tilde{e}$ is larger than that of SCS$\tilde{e}^-$. A closer analysis of $A$ values will explain this paradox and give a deeper insight into the bonding character
of the highest occupied \( \Pi(g)^{MO} \). A semiempirical method by Ishiguro and Kobori\(^{215} \) gave a very close estimate of \( A \) values for simple diatomic molecules. Their method should apply equally well to our linear molecules, especially in the \( ^2\Pi(g) \) ionic state, because the half filled MO of the ion is nonbonding (or nearly so) and has little contribution from the central carbon atom to make the two center contribution negligible\(^{215} \). The spin-orbit coupling constant can then be approximated\(^{215} \) by: 

\[
A = C_c^2\zeta_c + C_x^2\zeta_x + C_y^2\zeta_y
\]

where \( C's \) are the coefficients of the corresponding \( p_\pi \) atomic orbital in the highest occupied \( \Pi(g) \) MO and \( \zeta's \) are the corresponding atomic spin-orbit coupling constants. Because \( C_c \neq \zeta_c \neq 0 \), we can write \( A = C_x^2\zeta_x + C_y^2\zeta_y \). Using the observed \( A \) values we obtained \( \zeta_O = 0.020 \text{ eV}, \zeta_S = 0.055 \text{ eV} \) and \( \zeta_{Se} = 0.265 \text{ eV} \).

With these \( \zeta \) and appropriate \( A \) values, we obtain the following approximate wave function for the \( \Pi(g) \) MO:

\[
\psi_{\Pi} = \begin{bmatrix}
\text{OCS} \\
\text{OCSe} \\
\text{SCSe}
\end{bmatrix} = \begin{bmatrix}
-0.51 \, p_{\pi,0} + 0.86 \, p_{\pi, S} \\
-0.49 \, p_{\pi,0} + 0.87 \, p_{\pi, Se} \\
-0.62 \, p_{\pi,S} + 0.79 \, p_{\pi, Se}
\end{bmatrix}
\]

The greater contribution of the \( p_{\pi,Se} \) orbital, as indicated by the MO coefficients, in OCS than SCSe can be inferred directly from the larger difference in the orbital energies between O and Se than between S and Se and is the explanation for the larger \( A \) value of the \( \chi^2\Pi \) state of OCS\(^+\).
In view of the existence of the fifth band in the PE spectrum of CS$_2$, an effort has been made to find a similar band for the selenium compounds. If the photoionization cross section is not too small to evade the detection of the fifth band, as is most likely true, we then are led to the conclusion that the fifth band of CS$_2$ is not formed by an one-electron process, but by a two-electron one. This results in an ionic state whose electron configuration differs from that of the ground state of the neutral molecule by two (or more) MO's. This normally forbidden transition to a doubly-excited state of the molecular ion is allowed as a result of configuration interaction (section 2.2.4.a). The further clarification of this state must await future theoretical work.

Franck-Condon Factors and The Geometry of the Molecular Ion.

The vibrational Franck-Condon factors (FCF) for each ionic state have been measured and are listed in Table 10. The FCF's in the $X^2\Pi$ and $A^2\Pi$ states of OCSe$^+$ have not been measured because of severe overlap. The errors in these experimental FCF's vary considerably, and increase with the extent of overlap in the band. However, the qualitative feature, i.e., the intensity distribution, is not expected to change.

The measured FCF's have been used to estimate the geometry of each state of the molecular ion using the method
TABLE 10(a) Experimental and Calculated Franck-Condon Factors in the Individual States of CO\textsubscript{2}\textsuperscript{+}, CS\textsubscript{2}\textsuperscript{+} and CSe\textsubscript{2}\textsuperscript{+}

<table>
<thead>
<tr>
<th>Ionic state</th>
<th>Vibrational level</th>
<th>( \text{CO}_2^+ )</th>
<th>( \text{CS}_2^+ )</th>
<th>( \text{CSe}_2^+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n_1 ) ( n_2 ) ( n_3 )</td>
<td>Experimental</td>
<td>Calculated</td>
<td>Experimental</td>
</tr>
<tr>
<td>( ^2\Pi_{g} )</td>
<td>000</td>
<td>0.80</td>
<td>0.81</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.15</td>
<td>0.16</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>( \sim0.02 )</td>
<td>0.01</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>002</td>
<td>( \sim0.03 )</td>
<td>0.02</td>
<td>1.0</td>
</tr>
<tr>
<td>( ^2\Pi_{u} )</td>
<td>000</td>
<td>0.08</td>
<td>0.06</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.20</td>
<td>0.19</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.23</td>
<td>0.27</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.21</td>
<td>0.24</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>0.13</td>
<td>0.15</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>0.08</td>
<td>0.07</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>0.04</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>0.03</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>0.01</td>
<td>0.001</td>
<td>0.01</td>
</tr>
</tbody>
</table>
TABLE 10(a) (cont'd) Experimental and Calculated Franck-Condon Factors in the Individual States of $\text{CO}_2^+$, $\text{CS}_2^+$ and $\text{CSe}_2^+$

<table>
<thead>
<tr>
<th>Ionic state</th>
<th>Vibrational level</th>
<th>$\text{CO}_2^+$</th>
<th>$\text{CS}_2^+$</th>
<th>$\text{CSe}_2^+$</th>
<th>$\text{CO}_2^+$</th>
<th>$\text{CS}_2^+$</th>
<th>$\text{CSe}_2^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n_1$ $n_2$ $n_3$</td>
<td>Experimental</td>
<td>Calculated</td>
<td>Experimental</td>
<td>Calculated</td>
<td>Experimental</td>
<td>Calculated</td>
</tr>
<tr>
<td>900</td>
<td></td>
<td>0.07</td>
<td>0.061</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td></td>
<td>0.05</td>
<td>0.033</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1100</td>
<td></td>
<td>0.03</td>
<td>0.015</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td></td>
<td>0.02</td>
<td>0.006</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1300</td>
<td></td>
<td>0.01</td>
<td>0.002</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{B}^2\Sigma_u^+$</td>
<td>000</td>
<td>0.89</td>
<td>0.90</td>
<td>0.87</td>
<td>0.89</td>
<td>0.71</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.24</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>~0.01</td>
<td>&lt;0.01</td>
<td>~0.02</td>
<td>&lt;0.01</td>
<td>~0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>$\text{C}^2\Sigma_g^+$</td>
<td>000</td>
<td>0.88</td>
<td>0.91</td>
<td>0.87</td>
<td>0.85</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.06</td>
<td>0.06</td>
<td>0.11</td>
<td>0.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>002</td>
<td>0.06</td>
<td>0.03</td>
<td>~0.02</td>
<td>0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ionic state</td>
<td>Vibrational level</td>
<td>( \chi^2_\Pi )</td>
<td>( A^2_\Pi )</td>
<td>( \text{OCS}^+ )</td>
<td>( \text{OCSe}^+ )</td>
<td>( \text{SCSe}^+ )</td>
<td></td>
</tr>
<tr>
<td>-------------</td>
<td>------------------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>000</td>
<td>000</td>
<td>0.45</td>
<td>0.41</td>
<td>a) 0.78</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>001</td>
<td>001</td>
<td>0.27</td>
<td>0.27</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>002</td>
<td>002</td>
<td>( \approx 0.09 )</td>
<td>0.07</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>003</td>
<td>003</td>
<td>( \approx ) 0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>100</td>
<td>0.13</td>
<td>0.12</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>101</td>
<td>101</td>
<td>0.07</td>
<td>0.08</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>102</td>
<td>102</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
<td>200</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>201</td>
<td>201</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

TABLE 10(b) Experimental and Calculated Franck-Condon Factors in the Individual States of \( \text{OCS}^+ \), \( \text{OCSe}^+ \) and \( \text{SCSe}^+ \)
TABLE 10(b) (cont'd) Experimental and Calculated Franck-Condon Factors in the Individual States of OCS⁺, OCSe⁺ and SCSe⁺

<table>
<thead>
<tr>
<th>Ionic state</th>
<th>Vibrational level</th>
<th>OCS⁺</th>
<th>OCSe⁺</th>
<th>SCSe⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Experimental</td>
<td>Calculated</td>
<td>Experimental</td>
</tr>
<tr>
<td>004</td>
<td></td>
<td>0.04</td>
<td>0.036</td>
<td>0.10</td>
</tr>
<tr>
<td>005</td>
<td>Overlap with 200</td>
<td>0.013</td>
<td>0.10</td>
<td>0.12</td>
</tr>
<tr>
<td>006</td>
<td></td>
<td>0.004</td>
<td>0.11</td>
<td>0.15</td>
</tr>
<tr>
<td>007</td>
<td></td>
<td>0.11</td>
<td>0.16</td>
<td>0.08</td>
</tr>
<tr>
<td>008</td>
<td></td>
<td>0.11</td>
<td>0.14</td>
<td>0.06</td>
</tr>
<tr>
<td>009</td>
<td></td>
<td>0.10</td>
<td>0.11</td>
<td>0.03</td>
</tr>
<tr>
<td>0010</td>
<td></td>
<td>0.08</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>0011</td>
<td></td>
<td>0.07</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>0012</td>
<td></td>
<td>0.05</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>0013</td>
<td></td>
<td></td>
<td></td>
<td>0.015</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>0.05</td>
<td>0.047</td>
<td></td>
</tr>
<tr>
<td>101</td>
<td></td>
<td>0.10</td>
<td>0.102</td>
<td></td>
</tr>
<tr>
<td>102</td>
<td></td>
<td>0.10</td>
<td>0.107</td>
<td></td>
</tr>
<tr>
<td>Ionic state</td>
<td>Vibrational level</td>
<td>( n_1 )</td>
<td>( n_2 )</td>
<td>( n_3 )</td>
</tr>
<tr>
<td>-------------</td>
<td>------------------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>( 103 )</td>
<td></td>
<td>0.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 104 )</td>
<td></td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 105 )</td>
<td></td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 106 )</td>
<td></td>
<td>( \sim 0.01 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 200 )</td>
<td>( 005 + 200 )</td>
<td>( 0.06 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 201 )</td>
<td></td>
<td>0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 202 )</td>
<td></td>
<td>0.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 203 )</td>
<td></td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 204 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 300 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 301 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 302 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 303 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 304 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 10(b)(cont'd) Experimental and Calculated Franck-Condon Factors in the Individual States of OCS\(^+\), OCSe\(^+\) and SCSe\(^+\)**
TABLE 10(b) (cont'd) Experimental and Calculated Franck-Condon Factors in the Individual States of OCS$^+$, OCSe$^+$ and SCSe$^+$

<table>
<thead>
<tr>
<th>Ionic state</th>
<th>Vibrational level</th>
<th>OCS$^+$ Experimental</th>
<th>OCS$^+$ Calculated</th>
<th>OCSe$^+$ Experimental</th>
<th>OCSe$^+$ Calculated</th>
<th>SCSe$^+$ Experimental</th>
<th>SCSe$^+$ Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B^2\Sigma^+$</td>
<td>000 1.0</td>
<td>0.96</td>
<td>0.96</td>
<td>0.83</td>
<td>0.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>001 ~0.04</td>
<td>0.04</td>
<td>0.14</td>
<td>0.14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>002 ~0.03</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C^2\Sigma^+$</td>
<td>000 0.48</td>
<td>0.43</td>
<td>0.44</td>
<td>0.42</td>
<td>0.70</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>001 0.16</td>
<td>0.15</td>
<td>0.12</td>
<td>0.12</td>
<td>0.17</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>002 0.03</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 0.24</td>
<td>0.22</td>
<td>0.25</td>
<td>0.25</td>
<td>0.13</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>101 ~0.03</td>
<td>0.07</td>
<td>0.10</td>
<td>0.07</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>102 0.02</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>200 0.07</td>
<td>0.05</td>
<td>0.09</td>
<td>0.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>201 0</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>300 ~0.02</td>
<td>0.01</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) FCF was not measured because of severe overlap.
b) A single vibrational progression in $v_3$ was assumed.
outlined in section 2.2.3.c, the results are collected in Table 11. For comparison the geometries of two ionic states of \( \text{N}_2\text{O} \) have also been estimated using the FCF's reported by Turner et al \(^3\), and compared with the measured bond lengths. The estimated ionic geometries turned out to agree reasonably well with the available experimental ones, with a maximum deviation of 0.006 Å (Table 11). Unfortunately, the comparison is limited by available experimental data on ionic geometry. Guided by the initial success stated above, we might expect the results for the types of molecules studied here, i.e. linear triatomic molecules, would be reliable. The method used here together with the PES technique might provide a very general and convenient way of estimating ionic geometries. The test for the reliability of this method if applied to molecules of other symmetry species has to await future experimental data.

Several instructive conclusions can be drawn from the series of calculations: (1) Because of the criteria (section 2.2.3.c) used in determining the \( d \) values, we do not expect the calculated ionic geometry to be very much dependent on the accuracy of ionic vibrational frequencies. This means the frequencies determined by PES are accurate enough for the purpose although they normally have an error limit of 30 cm\(^{-1}\); (2) The method outlined in section 2.2.3.c assumes no mixing of normal coordinates of the same symmetry in going from the neutral to the ionic state, i.e., \( A_{ij} = \delta_{ij} \).
TABLE 11  Estimated Bond Lengths of the Individual States of \( \text{CO}_2^+ \), \( \text{CS}_2^+ \), \( \text{CSe}_2^+ \), \( \text{OCS}^+ \), \( \text{SCSe}^+ \), and \( \text{N}_20^+ \).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Electronic State</th>
<th>( d_1 \times 10^{20} ) ( \text{g}^{-1}\text{cm} )</th>
<th>( d_3 \times 10^{20} ) ( \text{g}^{-1}\text{cm} )</th>
<th>( \Delta r(\text{C-X}) ) ( \text{Å} )</th>
<th>( \Delta r(\text{C-Y}) ) ( \text{Å} )</th>
<th>( r(\text{C-X}) ) ( \text{Å} )</th>
<th>( r(\text{C-Y}) ) ( \text{Å} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2 )</td>
<td>( X^1\Sigma^+ )</td>
<td>0.124</td>
<td>0.124</td>
<td>0.017</td>
<td>0.017</td>
<td>1.162</td>
<td>1.162</td>
</tr>
<tr>
<td></td>
<td>( X^2\Pi^+ )</td>
<td>0.702</td>
<td>0.702</td>
<td>0.066</td>
<td>0.066</td>
<td>1.555</td>
<td>1.555</td>
</tr>
<tr>
<td>( \text{CO}_2^+ )</td>
<td>( A^2\Pi_u )</td>
<td>0.124</td>
<td>0.124</td>
<td>0.017</td>
<td>0.017</td>
<td>1.162</td>
<td>1.162</td>
</tr>
<tr>
<td></td>
<td>( B^2\Sigma^+ )</td>
<td>0.095</td>
<td>0.095</td>
<td>0.013</td>
<td>0.013</td>
<td>1.175</td>
<td>1.175</td>
</tr>
<tr>
<td></td>
<td>( C^2\Sigma^+ )</td>
<td>0.073</td>
<td>0.073</td>
<td>0.010</td>
<td>0.010</td>
<td>1.172</td>
<td>1.172</td>
</tr>
<tr>
<td>( \text{SCS} )</td>
<td>( X^1\Sigma^+ )</td>
<td>0.124</td>
<td>0.124</td>
<td>0.017</td>
<td>0.017</td>
<td>1.162</td>
<td>1.162</td>
</tr>
<tr>
<td></td>
<td>( X^2\Pi^+ )</td>
<td>0.702</td>
<td>0.702</td>
<td>0.066</td>
<td>0.066</td>
<td>1.555</td>
<td>1.555</td>
</tr>
<tr>
<td>( \text{SCS}^+ )</td>
<td>( A^2\Pi_u )</td>
<td>0.124</td>
<td>0.124</td>
<td>0.017</td>
<td>0.017</td>
<td>1.162</td>
<td>1.162</td>
</tr>
<tr>
<td></td>
<td>( B^2\Sigma^+ )</td>
<td>0.144</td>
<td>0.144</td>
<td>0.014</td>
<td>0.014</td>
<td>1.569</td>
<td>1.569</td>
</tr>
<tr>
<td></td>
<td>( C^2\Sigma^+ )</td>
<td>0.144</td>
<td>0.144</td>
<td>0.014</td>
<td>0.014</td>
<td>1.569</td>
<td>1.569</td>
</tr>
<tr>
<td>( \text{SeCS} )</td>
<td>( X^1\Sigma^+ )</td>
<td>0.124</td>
<td>0.124</td>
<td>0.017</td>
<td>0.017</td>
<td>1.162</td>
<td>1.162</td>
</tr>
<tr>
<td></td>
<td>( X^2\Pi^+ )</td>
<td>0.702</td>
<td>0.702</td>
<td>0.066</td>
<td>0.066</td>
<td>1.555</td>
<td>1.555</td>
</tr>
<tr>
<td>( \text{N}_20^+ )</td>
<td>( A^2\Pi_u )</td>
<td>1.425</td>
<td>1.425</td>
<td>0.088</td>
<td>0.088</td>
<td>1.799</td>
<td>1.799</td>
</tr>
</tbody>
</table>
### TABLE 11 (cont'd) Estimated Bond Lengths of the Individual States of $\text{CO}_2^+$, $\text{CS}_2^+$, $\text{CSe}_2^+$, $\text{OCS}^+$, $\text{SCSe}^+$, and $\text{N}_2\text{O}^+$.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Electronic State</th>
<th>$d_1 \times 10^{20}$</th>
<th>$d_3 \times 10^{20}$</th>
<th>$\Delta r (C-X)$</th>
<th>$\Delta r (C-Y)$</th>
<th>$r (C-X)^a$</th>
<th>$r (C-Y)^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SeCSe}^+$</td>
<td>$\chi^2 \Sigma_u^+$</td>
<td>0.324</td>
<td>0.324</td>
<td>0.020</td>
<td>0.020</td>
<td>1.731</td>
<td>1.731</td>
</tr>
<tr>
<td></td>
<td>$\chi^2 \Pi$</td>
<td>0.126</td>
<td>0.281</td>
<td>-0.024</td>
<td>0.074</td>
<td>1.136</td>
<td>1.634</td>
</tr>
<tr>
<td>$\text{OCS}^+$</td>
<td>$\chi^2 \Pi$</td>
<td>0.230</td>
<td>0.534</td>
<td>0.092</td>
<td>0.046</td>
<td>1.252</td>
<td>1.606</td>
</tr>
<tr>
<td></td>
<td>$\chi^2 \Sigma^+$</td>
<td>0.166</td>
<td>0.211</td>
<td>-0.039</td>
<td>0.069</td>
<td>1.121</td>
<td>1.629</td>
</tr>
<tr>
<td>$\text{OCSe}^+$</td>
<td>$\chi^2 \Pi$</td>
<td>0</td>
<td>1.170</td>
<td>0.031</td>
<td>0.181</td>
<td>1.190</td>
<td>1.890</td>
</tr>
<tr>
<td></td>
<td>$\chi^2 \Sigma^+$</td>
<td>0.048</td>
<td>0</td>
<td>-0.014</td>
<td>0.009</td>
<td>1.145</td>
<td>1.718</td>
</tr>
<tr>
<td></td>
<td>$\chi^2 \Sigma^+$</td>
<td>0.181</td>
<td>0.219</td>
<td>-0.048</td>
<td>0.067</td>
<td>1.111</td>
<td>1.776</td>
</tr>
<tr>
<td>$\text{SCSe}^+$</td>
<td>$\chi^2 \Sigma^+$</td>
<td>1.557</td>
<td>1.709</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 11 (cont'd) Estimated Bond Lengths of the Individual States of \( \text{CO}_2^+ \), \( \text{CS}_2^+ \), \( \text{CSe}_2^+ \), \( \text{OCS}^+ \), \( \text{SCSe}^+ \) and \( \text{N}_2\text{O}^+ \).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Electronic State</th>
<th>( d_1 \times 10^{20} ) g(^{-1})cm</th>
<th>( d_3 \times 10^{20} ) g(^{-1})cm</th>
<th>( \Delta r(\text{C-X}) ) Å</th>
<th>( \Delta r(\text{C-Y}) ) Å</th>
<th>( r(\text{C-X})^{a)} ) Å</th>
<th>( r(\text{C-Y})^{a)} ) Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{XCY} )</td>
<td>( \chi^2 \Pi )</td>
<td>0.115</td>
<td>0.161</td>
<td>-0.020</td>
<td>0.041</td>
<td>1.537</td>
<td>1.750</td>
</tr>
<tr>
<td></td>
<td>( \Lambda^2 \Pi )</td>
<td>0</td>
<td>1.054</td>
<td>0.063</td>
<td>0.104</td>
<td>1.620</td>
<td>1.813</td>
</tr>
<tr>
<td></td>
<td>( \text{B}^2 \Sigma^+ )</td>
<td>0</td>
<td>0.119</td>
<td>-0.007</td>
<td>-0.012</td>
<td>1.550</td>
<td>1.738</td>
</tr>
<tr>
<td></td>
<td>( \text{C}^2 \Sigma^+ )</td>
<td>0.122</td>
<td>0.234</td>
<td>-0.017</td>
<td>0.050</td>
<td>1.540</td>
<td>1.759</td>
</tr>
<tr>
<td>( \text{NNO} )</td>
<td>( \chi^1 \Sigma^+ )</td>
<td>0.190</td>
<td>0.238</td>
<td>-0.017</td>
<td>0.050</td>
<td>1.540</td>
<td>1.759</td>
</tr>
<tr>
<td>( \text{NNO}^+ )</td>
<td>( \chi^2 \Pi )</td>
<td>0.046</td>
<td>0.078</td>
<td>0.022</td>
<td>0.007</td>
<td>1.150(1.155)</td>
<td>1.191(1.185)</td>
</tr>
<tr>
<td></td>
<td>( \Lambda^2 \Sigma^+ )</td>
<td>0.063</td>
<td>0.131</td>
<td>0.011</td>
<td>-0.041</td>
<td>1.139(1.140)</td>
<td>1.143(1.141)</td>
</tr>
</tbody>
</table>

\( a) \) values in ( ) are experimental bond lengths from ref. 209
\( b) \) from ref. 209
\( c) \) from ref. 214
\( d) \) a single vibrational progression in \( \nu_3 \) was assumed.
in the exact expression $Q'_i = \Sigma A_{ij} Q''_j + d_i$. For molecules of $D_{\infty h}(C\chi_2)$ symmetry, no such assumption is necessary. Therefore, we expect the results for these molecules to be more reliable than those for molecules of $C_{\omega v}$ symmetry. This argument can further be extended to triatomic molecules of other symmetries. The reliability of the results would then be in this order $D_{\infty h} > C_{2v} > C_{\omega v} > C_s$, because the extent of coupling between normal vibrations of the totally symmetric species would normally increase in the same order; (3) In comparing the experimental and calculated FCF's (evaluated at the estimated geometry) in Table 10, we notice the agreement is much less satisfactory for the second bands where higher levels of vibrational excitation are involved. In particular, the calculated FCF's indicate a much narrower intensity distribution envelope. These discrepancies are understandable in view of the harmonic oscillator assumption. The unsatisfactory agreement is due to a poorer description of the vibrational function by harmonic wave functions at higher vibrational quantum numbers, whereas the more 'peaked' intensity distribution is due to the steeper slope of the harmonic potential compared to the true potential. An improvement in the method would be the inclusion of anharmonicity in the vibrational wave functions. (4) If the second band of OCSe were treated as a single progression in $v_3$ only, the estimated geometry would give an increase of 0.181 Å in $r$ (C-Se), which would be rather large. A smaller increase in $r$ (C-Se) would mean a less extensive progression. This result is consistent with
our assignment that more than one progression is involved in the band.

5.3 **Ozone (O₃)**

5.3.1 **Introduction**

The PE spectrum of O₃ has previously been recorded by Radwan and Turner²¹⁶ using a low resolution, retarding grid analyzer. Our study differs from theirs in that it is of much higher resolution and the measurements were made on a very pure O₃ sample (> 98%). Vibrational fine structure is now resolved in some bands and spurious bands due to the presence of residual oxygen can be unambiguously identified, thus enabling a more accurate determination of ionization potentials for O₃.

5.3.2 **Experimental**

The PE spectra were recorded with a nominal resolution of 20-25 meV (measured at FWHM of the argon doublet), and calibration was effected using both argon and oxygen peaks as markers. About 8 ml of ozonized oxygen (∼ 4% O₃) produced in a laboratory ozonizer was condensed, and the condensate pumped at -196°C down to a volume of about 1 ml which was then transferred to the Kel-F inlet system (section 3.3.4.b). The spectrometer was then pumped from
atmospheric pressure while keeping the O₃ sample at -196°C with the valve completely open. The operating vacuum was achieved in about an hour, by which time the amount of the residual oxygen should be negligible since at -196°C oxygen has a vapour pressure of ~130 mm Hg. The PE spectrum of ozone was then recorded with the sample held in an isopentane slush bath (-160°C) after regulating the pressure with the Kel-F valve.

The handling of O₃ adopted here involved the least disturbance of the sample and hence greatly reduced the hazard of an explosion. Furthermore, with the use of the direct inlet system, the decomposition of O₃ was found to be negligible and thus a study of pure O₃ was possible. The purity of the O₃ sample was checked by focussing on the first band of oxygen for at least 5 minutes and noting no detectable signal above the background. By repeating this process several times, we finally estimated the oxygen impurity to be less than 2% and we expect it to decrease as the experiment proceeded.

5.3.3 Results and Discussion

The HeI PE spectrum of O₃ is shown in Fig. 40. The first band has a peculiar contour which consistently showed up in two independent measurements separated in time by several days, with both the HeI (Fig. 41a) and NeI (Fig. 41b) light sources. The persistence of the band structure
FIGURE 40

IONIZATION POTENTIAL (eV)

Ar
FIGURE 41

b) Ne I

a) He I

IONIZATION POTENTIAL (eV)
rules out the possibility of either an autoionization process or an experimental artifact. In fact, upon close examination two bands can be identified and assigned to two independent ionization processes. The first IP has adiabatic and vertical values of 12.53 ± 0.01 and 12.75 ± 0.01 eV respectively, while the second IP appears to have an identical adiabatic and vertical value at 13.03 ± 0.02 eV. The first band exhibits six clearly resolved vibrational peaks, and beyond the sixth peak (ν' = 5) overlaps strongly with the second band. The vibrational spacing, unlike most cases, increases towards higher vibrational levels indicating a positive anharmonicity constant. With extensive averaging, the average vibrational spacing is found to be 630 cm⁻¹ with the first being 520 ± 30 cm⁻¹. This vibrational progression is assigned to the bending mode, ν₂, which is 705 cm⁻¹ in the molecular ground state, since the symmetric stretch ν₁, the other possible mode, is 1110 cm⁻¹ in the neutral molecule and would be expected to be much larger. Two additional peaks associated with the second IP can be identified (Fig. 41a) with an averaging spacing of 700 ± 50 cm⁻¹ which again can be assigned to the bending vibration. The third band is sharp and intense with an IP at 13.57 ± 0.01 eV, and definitely involves a rather extensive progression. It was, however, only possible to resolve some vibrational structure in some of the scans, thus rendering the vibrational analy-
sis of the band inconclusive. In favourable cases, a weak progression of $\sim 500 \text{ cm}^{-1}$ appeared, which, if real, would then probably correspond to the bending vibration. The fourth and fifth bands are both weak, broad and featureless centering at 17.8 eV and 20.3 eV respectively. Because of the fast rising background in the low electron kinetic energy region, the existence of these bands may not be entirely certain.

Contrasting our results with those of Radwan and Turner\textsuperscript{216} (Table 12), we note that the additional IP's given by them at 12.3, $\sim 17$ eV and $\sim 19.3$ eV are most probably due to oxygen while the other IP values agree very closely with ours. The first IP from PES is in accord with the value $12.8 \pm 0.1$ eV obtained by electron impact\textsuperscript{217} considering that the vertical IP is usually obtained from the latter technique. A recent photoionization study of ozone with mass anlysis\textsuperscript{218} gave the first IP at $12.67 \pm 0.02$ eV which is 0.14 eV higher than our adiabatic value. This large difference, which is far beyond the experimental error limit claimed, is perplexing since photoionization is a threshold phenomenon. In view of the experimental difficulty\textsuperscript{218}, we would be inclined to resolve this apparent discrepancy by suggesting that the transition to the first two cationic vibronic levels may be too weak to be detected in the photoionization study and the value 12.67 eV actually
TABLE 12  PES and Theoretical Data for $O_3$

<table>
<thead>
<tr>
<th>Ionic</th>
<th>Vertical IP (eV) from PES</th>
<th>IP (eV) from ab initio SCF MO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>$^2A_1$</td>
<td>12.75 ± 0.01 (12.53)*</td>
<td>12.52 ± 0.05</td>
</tr>
<tr>
<td>$^2A_2$</td>
<td>13.03 ± 0.02</td>
<td>12.3 ± 0.1 ?</td>
</tr>
<tr>
<td>$^2B_2$</td>
<td>13.57 ± 0.01</td>
<td>13.52 ± 0.05</td>
</tr>
<tr>
<td>$^2B_1$</td>
<td>17.8 ± 0.1</td>
<td>16.4 - 17.4 ?</td>
</tr>
<tr>
<td>$^2B_2$</td>
<td>19.24 ± 0.1</td>
<td>19.24 ± 0.1</td>
</tr>
<tr>
<td>$^2A_1$</td>
<td>20.3 ± 0.1</td>
<td></td>
</tr>
</tbody>
</table>

* adiabatic IP
corresponds to the \( v'_2 = 2 \) peak in the PE spectrum. For the first PE band, we further notice that the peaks beyond the \( v'_2 = 2 \) level broaden considerably. The broadening can be explained as due to the short lifetime of the ion in the higher vibronic levels as supported by Cook's measurement that the appearance potentials of the \( O_2^+ \) and \( O_5^+ \) ions are both at 12.67 eV, which, as pointed out above, corresponds to the \( v'_2 = 2 \) peak.

There are a number of accurate SCF MO calculations for the ground state of \( O_3 \) and the agreement among them is excellent. It is interesting to see what useful information these calculations provide. According to Rothenberg and Schaefer, who employed the most extensive basis set and obtained the lowest total energy, the orbital configuration of \( O_3 \) is:

\[
\ldots \ldots (2b_2)^2(4a_1)^2(5a_1)^2(3b_2)^2(1b_1)^2(4b_2)^2(6a_1)^2(1a_2)^2, \ \text{1A}_1
\]

They also studied the effect of d-orbital contribution and found that the ordering of MO energies is the same with and without them. Assuming Koopmans' theorem (KT), the IP's are calculated from the results of reference 219 and 221 and are collected in Table 12 for comparison. Considering that the calculated IP's are usually higher than the corresponding experimental values, we expect from the calculations five to six IP's accessible with HeI excitation. It seems then reasonable to assign three IP's to the PE bands between 12 and 14 eV and the rest to the fourth and
fifth bands. Direct application of KT to the MO results\textsuperscript{219,221} gives the ordering of the observed ionic states as \(X^2A_2\), \(A^2A_1\), \(B^2B_2\), \(C^2B_1\), \(D^2B_2\) and \(E^2A_1\). The long vibrational progression in the first band, however, indicates substantial geometry change, and is not likely to be associated with the non-bonding \(1a_2\) MO which is the antisymmetric combination of the end atom \(p^\pi\) functions. This is clearly manifested in Peyerimhoff and Buenker's work\textsuperscript{221} in which the angular dependence of orbital energies was studied and the energy of the \(1a_2\) orbital was found to have little angular dependence. In fact, by fitting the calculated Franck-Condon factors to the experimental ones (section 2.2.3.c), the bond angle and bond length of this ionic state were estimated to be 12° and 0.024 Å greater than that of the molecular ground state. Considering further that the failure of KT in predicting the correct ordering of states is more frequent when these states are close together, it would seem reasonable to believe KT is inapplicable in the present case and we would provisionally propose an interchange of cationic states relative to the KT ordering, i.e. the three lowest ionic states would be \(X^2A_1\), \(A^2A_2\) and \(B^2B_2\). The assignment proposed here is consistent with the predictions drawn from comparing the PE spectrum of \(O_3\) with that of \(NO_2\)\textsuperscript{109,222} and \(SO_2\)\textsuperscript{3,172}; all of these molecules have similar electronic structure. The bands associated with the corresponding
states in the three molecules show similar behaviour, namely, the length of the vibrational progression in each band is comparable from molecule to molecule, and decreases in the order of $^2A_1 > ^2B_2 > ^2A_2$, as expected from the respective bonding character of the orbitals involved. The long vibrational progression associated with the second ($^2B_2$) and third ($^2A_2$) IP's in $S_0^2$ is understandable in view of the far more important d-orbital participation in $S_0^2$ than in $O_3$ or $NO_2$.

The band separations in the PE spectrum of a neutral molecule should correlate with the electronic spectrum of its ion if due care is given to the fact that two-electron processes are normally forbidden in PES. Consequently, some of the ionic states observed in the electronic spectrum may not be accessible in photoionization and hence there may not always be a one-to-one correspondence between the corresponding PE and electron spectra. With this provision, it would be instructive to compare the electronic spectrum of $NO_2$, an isoelectronic species to $O_3^+$, with the PE spectrum of $O_3^+$. Comparisons of this type have been attempted for CP and $CS^+$ (section 4.1), $NH_2$ and $H_2O^+$ as well as $PH_2$ and $H_2S^+$. In these cases, the spectra for each pair of molecules are identical with respect to the ordering of electronic states, and are remarkably similar in the order of magnitude of the corresponding excitation energies. It seems, therefore, reasonable to expect a similar resemblance
between $O_3^+$ and $NO_2$. We note that the orbital configuration of $NO_2$ is:

\[ (3b_2)^2(1b_1)^2(4b_2)^2(1a_2)^2(6a_1)^1, 2A_1 \]

with the three highest occupied MO's arranged in the same order as the three lowest states of $O_3^+$ and that the ground state of $NO_2$ is $X^2A_1$. One $^2B_2$ state of $NO_2$ has recently been observed by Brand et al. to lie at 1.48 eV above the ground state and has been assigned as the lowest excited state. Unfortunately, no $^2A_2$ state has been identified for $NO_2$, probably because a forbidden transition is involved. A straightforward comparison between $O_3^+$ and $NO_2$ is thus impossible since the position of the unobserved $^2A_2$ state of $NO_2$ with respect to that of the $^2B_2$ state is not known. Yet some interesting inferences can be drawn by comparing the corresponding excitation energies if they can be assumed to be comparable. The first and second excitation energies (adiabatic) of $O_3^+$ are 0.50 and 1.04 eV respectively. Comparing these two values to 1.48 eV, we tend to believe that the new $^2B_2$ state of $NO_2$ is likely to correspond to the second excited state of $O_3^+$ rather than the first one. If this is the case, the second excited state of $O_3^+$ would be the $^2B_2$ state, and further, if the ordering of their respective electronic states is assumed to be the same, then the first excited state of $NO_2$ would be the $^2A_2$ state instead of the $^2B_2$ state as is the case proposed for $O_3^+$. 
In view of the apparent failure of KT in assigning the first IP of $O_2$, the validity of KT when applied to higher IP's is even more doubtful. Therefore, the assignment of the PE band at 17.3 eV to $1b_1$ and $3b_2$ ionizations, and that 20.3 eV to $5a_1$, based purely on MO results, is only tentative. Preliminary calculations by Herring et al.\cite{226} has suggested that the band at 17.8 eV may be due to CI states. If such is the case, the band at 20.3 eV would then be most likely due to ionizations from the orbitals $1b_1$, $3b_2$ and $5a_1$.

5.4 Nitrosyl Halides ($XNO$, $X = F, Cl, Br$)

5.4.1 Introduction

In spite of the fact that these are simple molecules, there is only a meager understanding of the electronic structure of the nitrosyl halides. This is presumably due to their instability and high reactivity, as exemplified by the fact that they are highly oxidizing. These molecules are increasingly unstable towards decomposition in the series $FNO$, $ClNO$, $BrNO$, such that $BrNO$ is very difficult to obtain in pure form (e.g. it is $\sim 7\%$ decomposed in the gas phase at room temperature). All of them attack many metals with $FNO$ being the most reactive.

This series of molecules is, moreover, of additional interest in view of the weak bonding between the halogen
atom and the NO radical, as reflected in their abnormally long N-X bond lengths\(^{227}\). This aspect has, in fact, been extensively discussed by Peyerimhoff and Buenker\(^{228}\) for the case of FNO.

5.4.2 Experimental

All three molecules were run using the stainless steel direct inlet (section 3.3.4.b) with the sample cooled and held in an appropriate temperature bath (FNO at \(-112^\circ\), ClNO at \(-78^\circ\) and BrNO at \(-63^\circ\)C). It was found necessary in all cases to use the differential pump to alleviate the problem of decomposition. Calibration of the spectra was effected using the argon doublet.

BrNO was prepared by reacting liquid Br\(_2\) with an excess of NO, which was finally pumped away. ClNO and FNO were both commercial products (Matheson and Ozark Mahoning respectively).

5.4.3 Results

The PE spectra of these molecules are shown in Fig. 42 and the IP's are gathered in Table 13.

**FNO** The PE spectrum of FNO (Fig. 42a) consists of three featureless bands. The first band starts at 12.66 eV and has its vertical IP at 12.94 eV. It is relatively sharp compared to the other two bands. The second band is broad extending over 2.4 eV, and has an intensity almost twice
FIGURE 42

Ionization Potential (eV)

(c) BrNO

(b) CINO

(a) FNO
TABLE 13  PES Data for the Nitrosyl Halides (XNO)

<table>
<thead>
<tr>
<th></th>
<th>FNO</th>
<th>CINO</th>
<th>BrNO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vertical IP (adiabatic) (eV)</td>
<td>Vertical IP (adiabatic) (eV)</td>
<td>Vertical IP (adiabatic) (eV)</td>
</tr>
<tr>
<td>1.</td>
<td>12.94 (12.66)</td>
<td>11.5 (10.94)</td>
<td>10.9 (10.7)</td>
</tr>
<tr>
<td>2.</td>
<td>14.5 (13.5)</td>
<td>11.5</td>
<td>10.9</td>
</tr>
<tr>
<td>3.</td>
<td>14.5</td>
<td>11.5</td>
<td>10.9</td>
</tr>
<tr>
<td>4.</td>
<td>18.5 (17.05)</td>
<td>16.15 (15.63)</td>
<td>15.12 (14.7)</td>
</tr>
<tr>
<td>5.</td>
<td>19.0</td>
<td>17.13 (16.95)</td>
<td>16.42 (15.8)</td>
</tr>
<tr>
<td>6.</td>
<td>19.5 (?)</td>
<td>18.97 (18.59)</td>
<td>17.41 (16.8)</td>
</tr>
<tr>
<td>7.</td>
<td>--</td>
<td>--</td>
<td>18.66 (18.0)</td>
</tr>
</tbody>
</table>
that of the first band. It commences at 13.5 eV and reaches its maximum at 14.5 eV. The third band is also broad and intense, with a spread of ca. 2 eV. The threshold and maximum of this band are at 17.85 and 18.5 eV respectively.

**CINO** The PE spectrum of CINO (Fig. 42b) shows four distinct bands with vibrational structure resolved on two of them. The first band is by far the most intense, with adiabatic and vertical IP's of 10.94 and 11.47 eV respectively. The second distinct band shows some vibrational fine structure, which disappears beyond the third component peak. The vibrational spacing averages 1380 ± 100 cm⁻¹. The adiabatic IP is at 15.63 eV while the vertical occurs at 16.15 eV. The third band extending from ca. 16.7 to 18.3 eV shows at least nine vibrational components, the spacing between them decreasing rapidly from 1370 to 930 cm⁻¹. The vertical IP is at 17.13 eV but the exact position of adiabatic IP at 16.95 eV is tentative because of a possible peak at 16.76 eV. The fourth band is featureless, with adiabatic and vertical IP's at 18.59 and 18.97 eV respectively. There is, in addition, a suggestion of an additional broad band at 13.8 eV, which is extremely weak relative to the other bands.

**BrNO** Although the PE spectrum of BrNO (Fig. 42c) is complicated by the presence of the bands due to Br₂ and NO, five bands of BrNO, all structureless, can be distinctly identified. The first band in the spectrum is due to a superimposition
of the bands of Br₂ and BrNO, which upon manual deconvolution gives the first band of BrNO (Fig. 42c) having adiabatic and vertical IP's at 10.17 and 10.9 eV respectively. In all respects, this band of BrNO is similar to the corresponding band of ClNO. The second band of BrNO is partially overlapped by the third band of Br₂, but its vertical IP can be confidently placed at 15.12 eV. The third band which is partly concealed by the intense peak of NO at 16.54 eV is estimated to have its vertical at 16.42 eV. The vertical IP's of the fourth and fifth bands are 17.41 and 18.66 eV respectively.

5.4.4 Discussion

To assist the assignment of the PE spectra, we have carried out CNDO type MO calculations for the nitrosyl halides. The results are collected in Table 14, which lists the symmetry, bonding character and energy of the individual MO. In addition, the ab initio calculations on FNO are also included. All these calculations consistently indicate that the individual nitrosyl halides can be described quite concisely as a loosely bound combination of a halogen atom and a NO radical. More specifically, the XNO molecule can be treated as a collection of unperturbed doubly occupied halogen atomic orbitals and NO MO's with one true MO, i.e. 7α', formed from an almost equal admixture of halogen np and NO 2π orbital character.
<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Bonding Character</th>
<th>FNO</th>
<th>IP(eV) = -(\Delta) energy</th>
<th>CIHO</th>
<th>BrNO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Perturbation(^a)</td>
<td>(^b)</td>
<td>CNDO/(^c)</td>
</tr>
<tr>
<td>7a'</td>
<td>(2\Pi)-NO(out of phase)+(p_x)-X</td>
<td>13.1</td>
<td>14.6</td>
<td>11.3</td>
<td>14.0</td>
</tr>
<tr>
<td>2a''</td>
<td>(p_y)-X</td>
<td>15.6</td>
<td>17.6</td>
<td>15.3</td>
<td>15.6</td>
</tr>
<tr>
<td>6a'</td>
<td>(p_z)-X</td>
<td>15.6</td>
<td>17.8</td>
<td>15.4</td>
<td>15.6</td>
</tr>
<tr>
<td>1a''</td>
<td>(1\Pi)-NO(in phase)</td>
<td>19.1</td>
<td>21.4</td>
<td>19.2</td>
<td>16.7</td>
</tr>
<tr>
<td>5a'</td>
<td>(5\sigma)-NO(in phase)</td>
<td>19.7</td>
<td>21.6</td>
<td>19.4</td>
<td>16.9</td>
</tr>
<tr>
<td>4a'</td>
<td>(1\Pi)-NO(in phase)</td>
<td>20.3</td>
<td>23.0</td>
<td>21.7</td>
<td>17.7</td>
</tr>
<tr>
<td>3a'</td>
<td>(4\sigma)-NO(out of phase)</td>
<td>23.5</td>
<td>27.8</td>
<td>24.8</td>
<td>26.9</td>
</tr>
</tbody>
</table>

\(^{a}\) ref. 227. \(^{b}\) ref. 228. \(^{c}\) ref. 76; all IP's with 4 eV adjustment. \(^{d}\) ref. 232
In addition to the correlations with these theoretical results, the assignment of the PE spectra should also invoke the following considerations:

1. In view of the localization of the halogen lone pairs, the reorganization energy is expected to be appreciable upon ionization. This is especially true for the fluorine lone pairs since a positively charged fluorine atom is particularly unstable, and thus tends to draw electrons from the NO moiety. Consequently, allowance for such an effect should be made when applying Koopmans' theorem to the theoretical results.

2. Since the electronic structures of the three molecules are closely related, qualitative considerations lead one to expect that bands in the spectrum of BrNO should be shifted to lower IP's relative to the corresponding bands in the spectrum of ClNO, which should, in turn, be lower than those of FNO.

Based upon these considerations and, in addition, the relative band intensities, the spectra of the nitrosyl halides can be satisfactorily assigned as follows:

FNO The first band is to be associated with the 7a' orbital (the only true MO), whereas the second band is due to the almost degenerate, highly relaxed F lone pairs, 2a'' and 6a'. While it is difficult to decide whether two or three IP's are to be associated with the third band, the band shape and
relative intensity tend to suggest that three IP's (1a'', 5a' and 4a') are occurring here. This conclusion is also supported by the ab initio calculation with perturbation corrections to Koopmans' theorem\textsuperscript{229} (Table 14).

ClNO The intense, first band is assigned to three IP's, the 7a' and the two Cl lone pairs, 2a'' and 6a'. The second, third and fourth bands are respectively due to 1a'', 5a' and 4a'. The vibrational structure observed in the second and third bands (1380 and 1200 cm\textsuperscript{-1} respectively) is a simple progression of $\nu_{NO}$ (1800 cm\textsuperscript{-1} in the neutral molecule\textsuperscript{230}).

The excitation of $\nu_{NO}$ and the decrease in frequency are to be expected in view of the bonding character of the respective MO's (Table 14). The sudden loss of the vibrational structure beyond $v' = 2$ in the second band is indicative of a dissociation process. The assignment of the weak band at 13.8 eV poses a problem. At the moment, we can only suggest several alternatives to explain this feature: - (1) The possibility of impurities is unlikely since the band exists with the same relative intensity in spectra obtained with different samples and its intensity appears to follow that of the other bands. (2) In view of the extremely weak intensity of the band and by comparing the individual spectra of the three nitrosyl halides, we do not expect a band arising from an 'allowed' single-step one-electron ionization to appear in this region. (3) Its
abnormal intensity and position tends to suggest that the band may be associated with a CI state.

**BrNO** Except for an additional band, the spectrum of BrNO is very similar to that of ClNO, and indeed it can be analyzed in a similar fashion. The first band is again due to three IP's, one from 7a' and two from the Br lone pairs, 2a'' and 6a', while other bands are successively assigned to 1a'', 5a', 4a' and 3a' orbitals.

The assignment of the bands due to the two halogen lone pairs to be part of the first band in the cases of ClNO and BrNO is supported by the following observations.

1. The region 12-14 eV in both cases is free of any bands that may be associated with Cl or Br lone pair IP's. As they are not anticipated to fall at an IP greater than 14 eV, they must have merged with the first (7a') band.
2. This is corroborated by the relative intensity of the first band in ClNO and 3rNO, suggesting that this band is associated with more than one IP.
3. In addition the trend of all the IP's from the F through the Cl to the Br substituted compounds (see correlation lines in Fig. 42) is what is anticipated for the halogen series on electronegativity grounds.

Comparing the IP's of the halogen lone pairs in these molecules (F = 14.5 eV, Cl = 11.5 eV and Br = 10.9 eV) to their respective valence orbital ionization potentials
(F = 18.7 eV, Cl = 13.7 eV and Br = 12.4 eV), one notes the large effect of reorganization upon ionization. The magnitude of this reorganization which is in the order, Br < Cl < F, is understandable on the basis of the difference of their electronegativities (Br < Cl < F), since the more electronegative halogen will tend to withdraw more electrons from the NO moiety, and thus gives rise to more reorganization upon ionization. In this respect, one has the case of FNO approaching the situation of F^+NO, thus resulting in an abnormally low IP (14.5 eV) for the F lone pairs, which are generally around 16 eV or higher (e.g. HF, the fluorine substituted methanes, SiF₄).

5.5 Nitric Acid (HNO₃) And Nitryl Halides (XNO₂, X = F, Cl)

5.5.1 Introduction

HNO₃ and its halogen substituted derivatives FNO₂ and ClNO₂ are extremely corrosive compounds and strong oxidants. They attack many metals and decompose readily. Hence, they appear to be appropriate contenders for the present spectrometer.

In view of the remoteness of the hydrogen atom from the NO₂ group in HNO₃ and the free rotation of the N-O(H) bond, the OH group may be quite concisely treated as a pseudo-halogen atom when the interaction between the OH and
The PE spectra of the three molecules are shown in Figure 43, and the experimental results are tabulated in
Figure 43

(a) HNO₃
(b) ClNO₂
(c) FNO₂

Ionization Potential (eV)

Intensity (Arbitrary Units)
Table 15.

$\text{HNO}_3$ The PE spectrum of $\text{HNO}_3$ (Fig. 43a) shows evidence for at least eight IP's. There is extensive vibrational structure in the region between 12.0 and 13.1 eV (Fig. 44a), which can be identified as arising from three bands. The first band has an adiabatic IP of 11.96 eV and a vertical IP of 12.39 eV corresponding to the seventh peak. The extensive vibrational progression with an average spacing of 560 cm$^{-1}$ probably corresponds to the ionization of a strongly bonding or antibonding electron. There is also strong evidence for another series starting at 1370 cm$^{-1}$. Here the vibrational spacing is again $\sim$ 560 cm$^{-1}$. Towards higher vibrational quantum number, the two series merge, and are then overlapped by the second and third bands. The second band (Fig. 44a) has an identical adiabatic and vertical IP of 12.49 eV and shows a simple progression with a fairly even spacing of 1060 cm$^{-1}$. The third band (Fig. 44a) resembles the second, with coincident adiabatic and vertical IP's at 12.63 eV. Here the vibrational series shows four discernible peaks, with once again a fairly even spacing of 1160 cm$^{-1}$. The fourth band with a coincident adiabatic and vertical IP at 13.23 eV is sharp and intense, most likely corresponding to the ionization of a nonbonding electron. This band shows a weak vibrational series with an average spacing of 840 cm$^{-1}$. The fifth band with a vertical
<table>
<thead>
<tr>
<th></th>
<th>PES</th>
<th>CNDO/2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vertical IP (adiabatic) (eV)</td>
<td>Vibrational frequency (cm⁻¹)</td>
</tr>
<tr>
<td>HNO₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>²A₁</td>
<td>12.39(11.96)</td>
<td>560,1370(?)</td>
</tr>
<tr>
<td>²A₂</td>
<td>12.49</td>
<td>1060</td>
</tr>
<tr>
<td>²B₂</td>
<td>12.63</td>
<td>1160</td>
</tr>
<tr>
<td>²B₁</td>
<td>13.23</td>
<td>840</td>
</tr>
<tr>
<td>²B₂</td>
<td>13.70(13.4)</td>
<td></td>
</tr>
<tr>
<td>²B₁</td>
<td>16.78(16.10)</td>
<td></td>
</tr>
<tr>
<td>²A₁</td>
<td>18.63(18.36)</td>
<td></td>
</tr>
<tr>
<td>²B₂</td>
<td>19.24(19.0)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CINO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>²B₂</td>
<td>12.08(11.84)</td>
<td>420</td>
</tr>
<tr>
<td>²B₁</td>
<td>12.08(11.84)</td>
<td>420</td>
</tr>
<tr>
<td>PES</td>
<td>CNDO/2</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>---------------------</td>
<td></td>
</tr>
<tr>
<td>Vertical IP</td>
<td>Vibrational</td>
<td>Orbital symmetry</td>
</tr>
<tr>
<td>(adiabatic)</td>
<td>frequency (cm⁻¹)</td>
<td></td>
</tr>
<tr>
<td>(eV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>²A₂</td>
<td>12.81(12.40)</td>
<td>1a₂</td>
</tr>
<tr>
<td>²A₁</td>
<td>13.25(13.01?)</td>
<td>5a₁</td>
</tr>
<tr>
<td>²B₂</td>
<td>13.62</td>
<td>3b₂</td>
</tr>
<tr>
<td>²B₁</td>
<td>18.1 - 19.6</td>
<td>1b₁</td>
</tr>
<tr>
<td>²A₁</td>
<td></td>
<td>4a₁</td>
</tr>
<tr>
<td>²B₂</td>
<td></td>
<td>2b₂</td>
</tr>
<tr>
<td>²A₂</td>
<td>13.51(13.09)</td>
<td>1a₂</td>
</tr>
<tr>
<td>²A₁</td>
<td>13.91</td>
<td>5a₁</td>
</tr>
<tr>
<td>²B₂</td>
<td>14.40(14.2)</td>
<td>4b₂</td>
</tr>
</tbody>
</table>
TABLE 15 (cont'd) PES and Theoretical Data for HNO<sub>3</sub>, ClNO<sub>2</sub> and FNO<sub>2</sub>

<table>
<thead>
<tr>
<th>PES</th>
<th>Vertical IP (adiabatic) (eV)</th>
<th>Vibrational frequency (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>CHNO/2</th>
<th>Orbital symmetry</th>
<th>Orbital energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3b&lt;sub&gt;2&lt;/sub&gt; (F-Pσ)</td>
<td>17.6(16.3)</td>
</tr>
<tr>
<td>2B&lt;sub&gt;2&lt;/sub&gt;</td>
<td>15.0 - 17.1</td>
<td></td>
<td></td>
<td>2b&lt;sub&gt;1&lt;/sub&gt; (F-Pπ)</td>
<td>17.8(16.9)</td>
</tr>
<tr>
<td>2B&lt;sub&gt;1&lt;/sub&gt;</td>
<td>18.5(18.0)</td>
<td></td>
<td></td>
<td>1b&lt;sub&gt;1&lt;/sub&gt;</td>
<td>23.4(23.0)</td>
</tr>
<tr>
<td>2A&lt;sub&gt;1&lt;/sub&gt;</td>
<td>18.9</td>
<td></td>
<td></td>
<td>4a&lt;sub&gt;1&lt;/sub&gt;</td>
<td>22.5(21.0)</td>
</tr>
<tr>
<td>2B&lt;sub&gt;2&lt;/sub&gt;</td>
<td>19.60</td>
<td>1000</td>
<td></td>
<td>2b&lt;sub&gt;2&lt;/sub&gt;</td>
<td>21.6(20.0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3a&lt;sub&gt;1&lt;/sub&gt;</td>
<td>25.9(24.7)</td>
</tr>
</tbody>
</table>

* Values in brackets are INDO results; all IP's with 4 eV adjustment.
IP at 13.70 eV is broad and structureless. The next three bands with vertical IP's at 16.78, 18.63 and 19.24 eV respectively are again structureless.

CINO$_2$ The PE spectrum of CINO$_2$ (Fig. 43b) shows five distinct bands. The first band (Fig. 44b) with a vertical IP at 12.08 eV is sharp, suggesting that the ionization of nonbonding electrons is involved. There is, however, some weak vibrational structure on this band, the average spacing between peaks being 420 cm$^{-1}$. The second band (Fig. 44b) with a vertical IP at 12.81 eV partially overlaps the third band and appears to have no structure. Because of this overlap, the adiabatic IP of the third band cannot be determined accurately, but is estimated at 13.01 eV. The vertical transition of the third band occurs at 13.25 eV, and the vibrational progression appears to be a simple series with an average spacing of 850 cm$^{-1}$. The fourth band at 13.62 eV, which partly overlaps with the third, appears to be structureless. The fifth band (Fig. 43b) at 18.7 eV separated by $\sim$ 4 eV from the first four bands, is fairly broad and intense, and thus probably corresponds to more than one IP.

FNO$_2$ The PE spectrum of FNO$_2$ (Fig. 43c) exhibits six distinct bands. The first three bands overlap one another, and are shown at higher resolution in Fig. 44c. The vertical transitions of these three bands are at 13.51, 13.91 and
a. \( \text{HNO}_3 \)

b. \( \text{CINO}_2 \)

c. \( \text{FNO}_2 \)

**Figure 44**
14.40 eV respectively. The overall shape of the first band definitely suggests the existence of some vibrational structure. However, because of the overlap from the second band, and the severe deterioration of resolution (presumably resulting from sample poisoning), it is impossible to be specific about the nature of this vibrational structure. Around the maximum of the second band a vibrational spacing of 1170 cm\(^{-1}\) is observed, but due to the overlap the 0-0 transition for this band cannot be measured. Judging from the FC envelope, this band appears to be fairly extensive, corresponding to the ionization of a fairly bonding or anti-bonding electron. The third band is quite sharp yet shows no structure. The fourth and fifth bands are both broad and featureless. The shape of the fifth band suggests that it may actually consist of two bands having vertical IP's of 18.5 and 18.9 eV respectively. The sixth band has an identical adiabatic and vertical IP of 19.60 eV and two higher vibrational peaks with an average spacing of 1000 cm\(^{-1}\).

5.5.4. Discussion

The assignments for the PE spectra of these molecules are assisted by correlation with the known levels of NO\(_2\), by consideration of the electronic effects of the X substituent, by using information from vibrational analysis, and by reference to the MO calculations.

The PE spectra of HNO\(_3\), ClNO\(_2\) and FNO\(_2\) (Fig. 43)
can be conveniently divided into two regions. The first region refers to bands lying between 12-16 eV, while the other region considers bands above 16 eV. If the NO₂ group and the X substituent may be considered as separate moieties as in the case of XNO (section 5.4), then from a qualitative point of view we expect to find in the HeI spectra of XNO₂ approximately eight IP's. They correspond roughly to the six IP's from the NO₂ group and the two IP's from the X substituent, which are respectively the number of MO's capable of being ionized by HeI radiation (21.22 eV) in the individual moieties. The actual number of IP's observed may differ from the expected eight if interactions between the NO₂ and X moieties results in a lowering or raising of some of the originally accessible IP's. Furthermore, using the same kind of qualitative consideration it seems safe to expect that in the first region of the spectra there will be three IP's resulting from the ionization of the highest occupied (a₁, a₂ and b₂) MO's of NO₂, and two further IP's from the X substituent, i.e. a total of five IP's below ca. 16 eV. The two IP's coming from the halogen group correspond to the nearly degenerate pσ(b₂) and pπ(b₁) lone pairs, and those for the OH group correspond to the single O lone pair and OH σ orbital.

The above expectations are corroborated by the CNDO/2 MO results (Table 15), in that the calculations
consistently predict that the individual spectra indeed separate into two regions with the first region having exactly five IP's. Furthermore, two of the first five IP's are mainly localized on X and the other three are predominantly from the NO₂ contribution.

Considering that the IP of the Cl lone pair in other Cl substituted compounds (Cl₂, CH₃Cl, ClNO etc.) normally falls between 11-12 eV, we may assign the first band (12.1 eV) of ClNO₂ to the essentially degenerate Cl lone pairs (4b₂ and 2b₁). The sharpness of the band is consistent with the nonbonding character of the lone pair orbitals, and the general shape suggests the almost complete superimposition of two IP's. The weak vibrational excitation of 420 cm⁻¹ may be assigned to the symmetric NO₂ bending mode, which is 411 cm⁻¹ in the neutral molecule. Similar considerations lead us to assign the broad band at 15.8 eV in FNO₂ to the two almost degenerate F lone pairs. The width of this band compared to that of the corresponding band of ClNO₂ may be accounted for by the dual facts that the two F lone pairs may have slightly different energies, and that appreciable reorganization occurs upon ionization. In the case of HNO₃, the sharp band at 13.23 eV is most likely due to the O lone pair (2b₁), while comparative energy considerations lead us to assign the featureless band at 13.70 eV to the OH σ orbital (3b₂). The energy separation (0.5 eV)
between these two IP's is surprisingly small compared to that of other OH containing compounds (e.g. 2.1 eV for H$_2$O).

The low value for the σ OH ionization may be explained by the fact that the bond between O and H is highly ionic as reflected in the strong acidity of H$_2$O$_3$, and thus less energy is required to remove an electron dwelling mainly on the O atom. On the other hand, the high IP for the O lone pair may be accounted for by the strong electron withdrawing ability of the NO$_2$ group. The vibrational structure (840 cm$^{-1}$) on the fourth band is most likely $v_2$ (The N-OH stretch), which is 886 cm$^{-1}$ in the neutral molecule.  

As discussed above, the three other bands in the first region correspond to the three lowest occupied orbitals ($a_1$, $a_2$ and $b_2$) of NO$_2$. In NO$_2$ itself, the relative ordering of these orbitals is $a_1 < a_2 \sim b_2$. The orbital $a_1$ is strongly bonding all over the NO$_2$ group, $a_2$ is the non-bonding, antisymmetric combination of O $p_\pi$ orbitals, and $b_2$ is antibonding. As a result, the PE band corresponding to the ionization of an electron from the $a_1$ orbital usually shows extensive vibrational structure. Taking this into account we are led to assign the first band (12.39 eV) of H$_2$O$_3$, the third band (13.25 eV) of ClNO$_2$ and the second band (13.91 eV) of FNO$_2$ to the $a_1$ ionization, since all of them show extensive vibrational structure. In view of the bonding character of the $a_1$ orbital, the 560 and 1370 cm$^{-1}$
vibrational intervals on the first band of HNO$_3$ are then assigned to $v_3$ (symmetric NO$_2$ bend) and $v_1$ (symmetric N-O stretch), the corresponding frequencies in the neutral molecule being 675 and 1320 cm$^{-1}$. Similarly, the 850 cm$^{-1}$ vibrational interval on the third band of ClNO$_2$ and the 1170 cm$^{-1}$ on the second band of FNO$_2$ are identified as $v_1$, which is 1293$^{235}$ and 1312$^{237}$ cm$^{-1}$ in the neutral states of ClNO$_2$ and FNO$_2$ respectively.

The relative ordering of the two remaining NO$_2$ type levels $a_2$ and $b_2$ presents somewhat of a problem, since in these cases vibrational analysis is not helpful. However, by reference to the calculations (Table 15), and by comparison with NO$_2$ itself, the $a_2$ level probably lies lower in energy than $b_2$. Consequently, the relative ordering of the NO$_2$ type levels is $a_1 < a_2 < b_2$ for HNO$_3$ and $a_2 < a_1 < b_2$ for ClNO$_2$ and FNO$_2$. In HNO$_3$ the vibrational structure associated with the second ($a_2$) and third ($b_2$) bands may be assigned to $v_1$ (1320 cm$^{-1}$ in the neutral molecule). The reverse ordering of the $a_1$ and $a_2$ levels in going from HNO$_3$ to ClNO$_2$ and FNO$_2$ is understandable in view of the electronic effects of the X substituents. Considering the bonding character of the $a_1$ and $a_2$ orbitals, we then expect the $a_2$ orbital (with no X character) to be the least perturbed, and the $a_1$ orbital to be appreciably affected. As a result, the $a_1$ orbital is more stable than the $a_2$ orbital in ClNO$_2$ and FNO$_2$. 
Definitive assignments for the bands in the second region (> 16 eV) of the PE spectra are difficult. By analogy with NO\textsubscript{2}\textsuperscript{109,222}, the tentative assignments are given in Table 15. In the second region, there are three bands in the spectra of HNO\textsubscript{3} and FNO\textsubscript{2}, while only one broad band is observed for ClNO\textsubscript{2}. Considering that the inductive effect of Cl is somewhere between that of OH and F, we should expect the same number of bands for ClNO\textsubscript{2}. This expectation is well satisfied if the band of ClNO\textsubscript{2} lying between 18.1 - 19.6 eV is actually due to three overlapping bands. The vibrational excitation (1000 cm\textsuperscript{-1}) on the last band (19.6 eV) of FNO\textsubscript{2} is identified as \nu_1 (1312 cm\textsuperscript{-1} in the neutral molecule), and is thus consistent with the strongly bonding character of the b\textsubscript{1} orbital.

Qualitative considerations of the ordering of the inductive effects of the substituents, i.e. OH < Cl < F, lead us to expect that the bands corresponding to the removal of electrons from orbitals mainly of NO\textsubscript{2} character should be shifted to higher IP's in the order HNO\textsubscript{3} < ClNO\textsubscript{2} < FNO\textsubscript{2}. That this condition is satisfied is illustrated in the correlation diagram shown in Fig. 45, which lends further support to the assignments proposed here.

In the light of the present study, it seems pertinent to make a few comments on the PE spectra of CH\textsubscript{3}NO\textsubscript{2}\textsuperscript{238}, which has similar electronic structure to the
molecules. First, in drawing an analogy between \( \text{NO}_2 \) and \( \text{CH}_3\text{NO}_2 \), Rabalais makes no mention of the bands that may be due to the \( \text{CH}_3 \) group. If this is done, then the six IP's observed would be all that should be expected in the PE spectrum of \( \text{CH}_3\text{NO}_2 \). However, by considering the smaller inductive effect of the \( \text{CH}_3 \) group compared to that of the \( \text{OH} \) group, and further, assuming the above considerations for the band positions to hold, we are tempted to suggest that two IP's have not been identified in the HeI PE spectrum of \( \text{CH}_3\text{NO}_2 \) (Fig. 45). Moreover, the existence of two additional IP's are further suggested by the INDO MO calculations, which predicts eight IP's below 21 eV for \( \text{CH}_3\text{NO}_2 \). Secondly, the assignment of the third band in the spectrum of \( \text{CH}_3\text{NCO} \) at 14.73 eV as due to the \( 4b_2 \) ionization conflicts with our qualitative picture, and thus appears to be unrealistic since the \( ^2B_2 \) state of \( \text{CH}_3\text{NO}_2^+ \) lies higher in energy than in any other related \( X\text{NO}_2 \) molecule as shown in Fig. 45. In this respect, we also note that the calculations (Table 15 and ref. 233) predict the \( \text{NO}_2 \) type \( b_2 \) orbital in \( \text{CH}_3\text{NO}_2 \) has the smallest absolute energy in the \( X\text{NO}_2 \) series. In view of these apparent discrepancies, the following amendments may be proposed: In order for the spectrum of \( \text{CH}_3\text{NO}_2 \) to correlate well with those of the other \( X\text{NO}_2 \) molecules (Fig. 45), two additional IP's are required. Inspection of Rabalais' spectrum suggests one additional band may be
IONIZATION POTENTIAL (eV)

NO₂
CH₃NO₂
HONO₂
CINO₂
FNO₂

\[ \begin{array}{cccccccc}
11 & 12 & 13 & 14 & 15 & 16 & 17 & 18 & 19 & 20 & 21 \\
\hline
1A & 3A & \frac{1B}{3B_1} & \frac{1B}{3B_2} & \frac{1B}{3B_3} & 3A_2 & 2A_2 & 2B_2 & 2B_1 & \frac{2B_1}{2B_2(2)} & \frac{2B_1}{2B_2(2)} & \frac{2B_1}{2B_2(2)} & \frac{2B_1}{2B_2(2)} \\
\end{array} \]
found underneath the first or second band, and another under the strong third or fourth band. The first of these two new bands would then be identified as due to the $4b_2$ level. The assignments for the five bands above 14 eV would be facilitated by the identification of bands due to the CH$_3$ group as in the case of other XNO$_2$. By comparison with CH$_4$ and the methyl halides, the bands corresponding to ionization from the CH$_3$ group probably lie between 14-16 eV. With these amendments the resulting assignments for the spectrum of CH$_3$NO$_2$ are shown in Fig. 45, and indicate satisfactory correlation with the other molecules. It is further noted that the proposed assignments are also in complete agreement with the calculations.
CHAPTER SIX

CONCLUSION

The results presented in this study have shown that the PE spectrometer can be successfully used to study transient species and reactive molecules, and that PES provides invaluable information on the molecular electronic structure of these systems, information that is difficult to obtain by any other spectroscopic techniques. Work is in progress to extend the range of transient species that can be studied by this technique. In this respect, we note that the principal requirement for a successful study is the formation of a sufficient concentration of the species of interest in the ionization region. The ultimate concentration of the species is mainly limited by its lifetime and the efficiency with which the species is produced. The limitation imposed by the lifetime can usually be alleviated by fast pumping, forming the species into a molecular beam, or by producing the species right in the ionization region. This leaves the efficiency of producing the species as the crucial factor for a successful study. Thus, the spectra
of the atomic species O, N, H and F (section 3.4) have been obtained whereas, those of BF and HNO, which have longer lifetimes, have so far evaded our detection. In addition to the sensitivity of the PE spectrometer, the lowest limit of the necessary concentration for detection is further determined by the photoionization cross section of the species, and by the extent of overlap in the PE spectrum. This latter point may be serious in systems in which we are trying to produce modifications by, say, discharge or pyrolysis, and where the products and reactants have IP's of similar energies. However, under favorable conditions, concentrations as low as a few per cent (as in the case of N atoms) may be detected.

Work is also in progress to use the high temperature pyrolysis unit (section 3.3.4.d) and the variable temperature unit (section 3.3.4.e), which have so far been only tested, to study some practical systems. For the high temperature unit, the following projects are presently underway.

1. \( \text{S}_3 \rightarrow \text{S}_2 \) (800°C) (ref. 239)

2. \( \text{CCl}_4 \rightarrow \text{CCl}_3 \) (800°C) (ref. 240)

3. \( \text{CBr}_4 \rightarrow \text{CBr}_3 \) (800°C) (ref. 240)

\( \rightarrow \text{CBr}_2 \) (1200°C) (ref. 241)
The study of the equilibrium between \( \text{NO}_2 \) and \( \text{H}_2\text{O}_4 \) at variable temperature is proceeding, as well as work on the conformational analysis of oxalyl halides\(^{244}\) by the use of the variable temperature unit.

The present study has also revealed a further aspect of PES which merits immediate attention, i.e. the use of PES for in-situ analysis of dynamic chemical systems. The potential of PES for such studies has been exemplified in the study of the systems of \( \text{SO-S}_2\text{O-SO}_2 \) (section 4.2) and \( \text{N}_2\text{H}_2-\text{NH}_3-\text{HCl} \) (section 4.4). With a knowledge of the (relative) photoionization cross sections of molecules (which may also be available by specific PE studies), such analysis by PES can be quantitative as well as qualitative. The capability of continuously monitoring the system of interest, together with the simplicity and speed of the operation is a great advantage, and PES promises to be a potential tool for analysis of such dynamic systems.

In the study of transient species, the positive identification of the bands due to species of interest is usually a problem, since other species are also present by virtue of the methods of production. The techniques that can be applied in this respect involve comparison
with molecules of similar electronic structure (e.g. S\(2\)),
with MO calculations, the judicial use of the chemical properties of the species (e.g. \(N_2H_2\)), and methods of producing the species by alternative routes to be certain of identification (e.g. \(S_2O, N_2H_2\)). Even so, unequivocal identification of the molecule is very often difficult. A further advance would be the use of the mass spectrometer in conjunction with the PE spectrometer to detect the molecular ions in coincidence with the photoelectrons. This would greatly simplify the procedure, and enable one to be certain of the origin of an electron of a particular energy.
REFERENCES


43. Commercial spectrometers are manufactured in U.S.A. by McPherson Instrument Corp. and Hewlett-Packard Co.; in Britain by Perkin-Elmer Corp., A.E.I. Ltd. and Vacuum Generators Ltd.; and in Japan by Japan Applied Spectroscopy Co.


49. T. Koopmans, Physica 1, 104 (1933).


103. G. Berthier, in Molecular Orbitals in Chemistry, Physics and Biology (P. O. Löwdin and B. Pullman, eds.),

120. E. A. Hylleraas. Z. Physik 48, 469 (1928).
141. E. M. Purcell, Phys. Rev. 54, 813 (1938).


154. After the completion of this work, a similar study was also reported by N. Jonathan, A. Morris, M. Okuda, K. J. Ross and D. J. Smith, Faraday Discussions 54, 48 (1972).


156. Marcel Horani, Private Communication.


162. C. E. Moore, Ionization Potentials and Ionization Limits Derived from the Analysis of Optical Spectra. NSRDS-NBS 34, Sept. 1970


164. Ref. 2, Appendix D.


197. E. Lindholm, Arkiv für Fysik 40, 97 (1953).
224. R. N. Dixon, G. Duxbury, M. Horani and J. Rostas,


226. F. G. Herring, private communication.


229. D. P. Chong, F. G. Herring and D. Williams, to be published.


APPENDIX

THIS PROGRAM CALCULATES FRANCK-CONDON FACTORS USING HARMONIC OSCILLATOR APPROXIMATION BY THE PROCEDURE OUTLINED IN SECTION 2.3.3 IN THIS THESIS.

REFERENCES:

PROGRAM WRITTEN BY SHUIT-TONG LEE IN 1972 AT THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF BRITISH COLUMBIA

INPUT DATA
1ST CARD IDENTIFICATION (20A4)
2ND CARD (3(F15.7,5X),2I2)
1ST ENTRY VIBRATIONAL FREQUENCY OF THE MOLECULE IN WAVE NO.
2ND ENTRY VIBRATIONAL FREQUENCY OF THE ION IN WAVE NO.
3RD ENTRY CHANGE IN NORMAL COORDINATE IN (GM**0.5*CM*10D20), IF EQUAL TO 0, IT IS INITIALIZED INTERNALLY,
SEE 5TH ENTRY BELOW
4TH ENTRY MAX NO. OF VIBRATIONAL PEAKS FOR WHICH CALC IS DONE.....MAX NO. = 16
5TH ENTRY ID = 2 RATIO OF V = 2 TO V = 1 IS USED TO CALCULATE THE CHANGE IN NORMAL COORD.
ID = 1 RATIO TO V = 1 TO V = 0 IS USED TO CALCULATE THE CHANGE IN NORMAL COORD.
ID = 0 BOTH CASES ABOVE ARE CALCULATED AND THEIR MEAN IS TAKEN.
3RD CARD READ IN EXPERIMENTAL FRANCK-CONDON FACTOR (8(10D4))
4TH CARD (I2,3X,F12.8,2X,I2)
1ST ENTRY NO OF INCREMENT
2ND ENTRY STEP OF INCREMENT
3RD ENTRY THE NO OF THE MOST INTENSE PEAK MAXVIB= VIB NO + 1
IF MAXVIB = 0 FRANCK-CONDON FACTORS ARE CALCULATED, OTHERWISE RATIO OF FCF ARE CALCULATED

DOUBLE PRECISION BETA,GAMA,X,Y,Z,RFCF,FCF,A,TEST,ERROR
DIMENSION RFCF(20),FCF(20),IDEN(20),TEST(20)
READ(5,10) (IDEN(I), I=1,20)
WRITE(6,20) (IDEN(I),I=1,20)
10 FORMAT(20A4)
20 FORMAT('1',1$' FRANCK-CONDON FACTORS OF THE MOLECULE',2X,20A4//)
READ (5,30) FREQM,FREQI,D,NOVIB,10
WRITE(6,40) FREQM,FREQI,D,NOVIB
30 FORMAT(3(F15.7,5X),2I2)
40 FORMAT(' MOLECULAR VIB FREQ = ',F7.2,'CM-1',10X, 
'ION VIB FREQ = ',F7.2,'CM-1'//' CHANGE IN NORMAL COORDINATE = ', 
2F7.4//' MAX VIB PEAK CALCULATED = ',12//)
READ(5,600) (TEST(I),I=1,16)
600 FORMAT(8D10.4).
WRITE(5,80) N,DINC,MAXVIB
80 FORMAT(I2,3X,F12.8,2X,I2)
WRITE(6,90) N,DINC
90 FORMAT(' NO OF INCREMENT = ',I2/' STEP OF INCREMENT = ',F7.4//)
BETA=FREQM/FREQI
X=1.-BETA
Y=1.+BETA
IF (D.GT.0.0) GO TO 159
D1=0.0
D2=0.0
TEST1=TEST(1)
TEST2=TEST(2)
TEST3=TEST(3)
IF (IO.EQ.2) GO TO 31
R=SQRT(TEST2/TEST1)
Z=R*Y/SQRT(2.)
D1=Z/(BETA*0.1336466*SQRT(FREQI))
IF (IO.NE.0) GO TO 61
31 R=SQRT(TEST3/TEST2)
S=R**2*Y**2-2*X
Z=(R*Y+SQRT(S))/2.
D2=Z/(BETA*0.1336466*SQRT(FREQI))
61 D=(D1+D2)/2.
159 DO 1000 K=1,N
IF (K .GT. N) GO TO 1100
IF (K .EQ. 1) GO TO 160
D=D+DINC
160 WRITE(6,95)  D
95 FORMAT(* CHANGE IN NORMAL COORDINATE = ',F7.4///)
GAMA=0.1336466*SQRT(FREQI)*D
Z=BETA*GAMA
I=1
RFCF(1)=1.*
I=I+1
IF (I .GT. NOVIB) GO TO 800
RFCF(2)=2.*Z**2/Y**2
I=I+1
IF (I .GT. NOVIB) GO TO 800
RFCF(3)=(2.*Z**2/Y)**2/(2.*Y**2)
I=I+1
IF (I .GT. NOVIB) GO TO 800
RFCF(4)=(2.*Z**3/Y+3.*X*Z)**2/(3.*Y**4)
I=I+1
IF (I .GT. NOVIB) GO TO 800
RFCF(5)=(16.*Z**4/Y**2+48.*Z**2*X/Y+12.*X**2)**2/(24.*16.*Y**4)
I=I+1
IF (I .GT. NOVIB) GO TO 800
RFCF(6)=(32.*Z**5/Y**2+160.*Z**3*X/Y+120.*X**2)**2/
1 (120.*32.*Y**6)
I=I+1
IF (I .GT. NOVIB) GO TO 800
RFCF(7)=(64.*Z**6/Y**3+480.*Z**4*X/Y+120.*X**2)**2/(720.*64.*Y**6)
I=I+1
IF (I .GT. NOVIB) GO TO 800
RFCF(8)=(128.*Z**7/Y**3+1344.*Z**5*X/Y**2+3360.*Z**3*X**2)**2/
1 (5040.*128.*Y**8)
I=I+1
IF (I .GT. NOVIB) GO TO 800
RFCF(9) = (256.*Z**8/Y**4+3584.*Z**6*X/Y**3+13440.*Z**4*X**2/Y**2 
+13440.*Z**2*X**3/Y+1680.*X**4)**2/(40320.*256.*Y**8) 
\[\text{I=I+1}\]

IF (I .GT. NOVIB) GO TO 800

RFCF(10) = (512.*Z**9/Y**5+49216.*Z**7*X/Y**4+48384.*Z**5*X**2/Y**3 
+80640.*Z**3*X**3/Y+30240.*Z*X**4)**2/(362880.*512.*Y**10) 
\[\text{I=I+1}\]

IF (I .GT. NOVIB) GO TO 800

RFCF(11) = (1024.*Z**10/Y**6+23040.*Z**8*X/Y**5+161280.*Z**6*X**2/Y**4 
+806400.*Z**4*X**3/Y**3+302400.*Z**2*X**4/Y**2+30240.*X**5)**2/(3628800.*1024.*Y**12) 
\[\text{I=I+1}\]

IF (I .GT. NOVIB) GO TO 800

RFCF(12) = (2.048D3*Z**11/Y**5+5.632D4*Z**9*X/Y**4+1.50688D5*Z**7*X**2/Y**3 
+1.77408D6*Z**5*X**3/Y**2+80640.*Z**3*X**4/Y+30240.*X**5)**2/(3.99168D7*2.048D3*Y**13) 
\[\text{I=I+1}\]

IF (I .GT. NOVIB) GO TO 800

RFCF(13) = (4.096D4*Z**12/Y**6+1.35168D5*Z**10*X/Y**5+1.52064D6*Z**8*X**2/Y**4 
\[\text{I=I+1}\]

IF (I .GT. NOVIB) GO TO 800

RFCF(14) = (8.192D3*Z**13/Y**7+3.19488D5*Z**11*X/Y**6+1.39296D7*Z**9*X**2/Y**5 
\[\text{I=I+1}\]

IF (I .GT. NOVIB) GO TO 800

RFCF(15) = (1.6384D4*Z**14/Y**8+7.45472D5*Z**12*X/Y**7+1.2300288D7*Z**10*X**2/Y**6 
+4.225216D7*Z**8*X**3/Y**5+1.50688D5*Z**6*X**4/Y**4+8432384D8*Z**4*X**5/Y**3+98336D6*Z**2*X**6/Y+6.65280D5*X**7)**2/(8.71782912010*1.6384D4*Y**19) 
\[\text{I=I+1}\]

IF (I .GT. NOVIB) GO TO 800

RFCF(16) = (3.276804Z**15/Y**9+1.72032D6*Z**13*X/Y**8+1.354624D7*Z**11*X**2/Y**7+3.075072D8*Z**9*X**3/Y**6+2.90594304D9*Z**7*X**4/Y**5+3.4216472D9*Z**5*X**5/Y**4+5.189184D8*Z**3*X**6/Y+5.189184D8*Z**7)**2/(1.307674368D12*3.276804*Y**20) 
\[\text{WRITE (69,99)}\]

99 FORMAT(* FRANCK-CONDON FACTORS*/) 

600 DO 200 I=1,NOVIB 

J=I-1 

WRITE(6,100) J,RFCF(I) 

100 FORMAT(' RFCF(',12') = ',D11.4) 

200 CONTINUE 

IF(MAXVIB.NE.0) GO TO 560 

A=0.0DO0 

DO 400 I=1,NOVIB 

A=A+RFCF(I) 

400 CONTINUE
WRITE(6,410) A
410 FORMAT(//' SUM OF RFCF = ',D11.4//)
GO TO 550
560 A=RFCF(MAXVIB)
M=MAXVIB-1
WRITE(5,570) M, A
570 FORMAT(//' RFCF(',I2,') =',D11.4,3X,' IS TAKEN AS THE REFERENCE'//)
WRITE(6,520)
520 FORMAT(6X,'CALCULATION',16X,'EXPERIMENT'//)
550 DO 500 I=1,NOVIB
J=I-1
FCF(I)=RFCF(I)/A
WRITE(6,510) J,FCF(I),TEST(I)
510 FORMAT( 'FCF(',I2,') = ',D11.4,10X,D11.4)
500 CONTINUE
CCC STANDARD DEVIATION=ERROR IS USED AS A CRITERION FOR THE BEST FIT
ERROR=0.0000
DO 900 I=1,NOVIB
ERROR=ERROR+(FCF(I)-TEST(I))**2
900 CONTINUE
WRITE(6,910) ERROR
910 FORMAT(//' STANDARD DEVIATION = ',D11.4)
1000 CONTINUE
1100 STOP
END


