ELECTRON SPECTROSCOPY USING
METASTABLE HELIUM ATOMS (21S, 23S)
AND 584 Å PHOTONS

by

DEREK SUI CHANG YEE


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

UNIVERSITY OF BRITISH COLUMBIA
October, 1975.
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
2075 Wesbrook Place
Vancouver, Canada
V6T 1W5

Date Dec 25/1975
ABSTRACT

Using a high resolution 127 degree electron analyzer, a quantitative comparison has been made of the He*\(^{(2^1S,2^3S)}\) Penning electron and the 584 Å photoelectron spectra of thirty molecules (H\(_2\), HD, D\(_2\), N\(_2\), CO, NO, O\(_2\), NH\(_3\), PH\(_3\), C\(_2\)H\(_4\), HCN, (CN)\(_2\), CH\(_3\)CN, BrCN, ICN, H\(_2\)O, CH\(_3\)OH, CH\(_3\)CH\(_2\)OH, (CH\(_3\))\(_2\)CHOH, (CH\(_3\))\(_3\)COH, CH\(_3\)OCH\(_3\), CH\(_2\)OCH\(_2\), CH\(_3\)CH\(_2\)OCH\(_2\)CH\(_3\), CH\(_2\)CH\(_2\)OCH\(_2\)CH\(_2\), OCH\(_2\)CH\(_2\)OCH\(_2\)CH\(_2\), HCHO, CH\(_3\)CHO, CH\(_3\)COCH\(_3\), HCOOH and CH\(_3\)COOH).

Where vibrational structure has been resolved, the vibrational spacings are observed to be the same (within experimental error) for both modes of ionization. In addition, the relative vibrational intensities for ionic states of the diatomic molecules (except for O\(_2\)) were found to be the same for both modes of ionization. For the process He*\(^{(2^3S)}\)/O\(_2\)\(^+(\tilde{X}^2Π_g^-)\), an observed difference of the vibrational envelope for He*\(^{(2^3S)}\) Penning ionization and 584 Å photoionization has been traced to an autoionizing level of O\(_2\) which is essentially resonant with the He*\(^{(2^3S)}\) metastable energy. Differences between the vibrational envelopes for Penning ionization and photoionization have also been observed for the ground ionic state of a number of oxygen containing molecules. These differences have been explained by perturbations of the potential surface of the target molecule due to the presence of the metastable atom.
When comparing the relative electronic state populations for the two modes of ionization, large differences were observed. Some of the difference has been explained by the fact that the state populations are a function of the excitation energy, since comparisons were made between photons with the energy 21.22 eV and metastable atoms with the energies 20.62 eV and 19.82 eV. For the \(-\text{C}=\text{N}\) containing molecules it was observed that the ratios of the relative populations of states corresponding to the removal of \(\pi\) bonding to nitrogen lone pair were significantly greater for photoionization than for Penning ionization.

Finally, the energy shifts \(\Delta E_{\text{obs}}\) were measured for the \(\text{He}^*(2^1S,2^3S)\) Penning ionization process. When vibrational structure was apparent in the electron spectra, it was possible to evaluate the true \(\Delta E\) energy shift from \(\Delta E_{\text{obs}}\). The magnitude of the true \(\Delta E\) energy shift was found to be of thermal energies.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter One</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1. Chemi-ionization Reactions</td>
<td>1</td>
</tr>
<tr>
<td>1.2. Experimental Methods for Chemi-ionization Studies</td>
<td>3</td>
</tr>
<tr>
<td>1.2.1. Analysis of the Ions</td>
<td>3</td>
</tr>
<tr>
<td>1.2.2. Analysis of the Electrons</td>
<td>6</td>
</tr>
<tr>
<td>1.3. Excited Atoms and Molecules</td>
<td>7</td>
</tr>
<tr>
<td>1.3.1. Introduction</td>
<td>7</td>
</tr>
<tr>
<td>1.3.2. Production and Quenching of Metastables</td>
<td>11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter Two</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionization Processes</td>
<td>14</td>
</tr>
<tr>
<td>2.1. Photoionization</td>
<td>14</td>
</tr>
<tr>
<td>2.1.1. Introduction</td>
<td>14</td>
</tr>
<tr>
<td>2.1.2. Franck-Condon Principle</td>
<td>15</td>
</tr>
<tr>
<td>2.1.3. Autoionization</td>
<td>18</td>
</tr>
<tr>
<td>2.2. Penning Ionization</td>
<td>19</td>
</tr>
<tr>
<td>2.2.1. Qualitative Description</td>
<td>19</td>
</tr>
<tr>
<td>2.2.2. Potential Curve Model</td>
<td>22</td>
</tr>
<tr>
<td>2.2.3. Quantum Mechanical Treatment of the Potential Curve Model</td>
<td>29</td>
</tr>
</tbody>
</table>
2.2.4. Penning Electron Spectra of Molecules ........................................... 31
   a. Shape of the Vibrational Envelope ............................................. 31
   b. Relative Electronic State Populations ........................................... 33
   c. Energy Shifts .......................................................... 36

CHAPTER THREE

Experimental .......................................................... 38
   3.1. Introduction ..................................................... 38
   3.2. The Spectrometer ............................................. 38
       3.2.1. Metastable Source ........................................... 38
       3.2.2. Collision Region ........................................... 41
       3.2.3. Electron Analyzer ........................................... 42
       3.2.4. Electron Detection ........................................... 45
       3.2.5. Light Source ................................................... 45
       3.2.6. Vacuum System ............................................. 48
   3.3. Treatment of Data ............................................. 50
       3.3.1. Energy Calibration ........................................... 50
       3.3.2. Electron Analyzer Transmission Function ....................... 50
       3.3.3. Background Subtraction Technique ............................... 51
   3.4. Sample Purity .................................................. 53

CHAPTER FOUR

Diatomic Molecules .................................................. 55
### Chapter Three
3.1. Introduction ................................................. 55
3.2. Molecular Hydrogen, Deuterium Hydride and Molecular Deuterium .......... 56
3.3. Molecular Nitrogen ........................................... 62
3.4. Carbon Monoxide ............................................. 68
3.5. Nitric Oxide .................................................... 74
3.6. Molecular Oxygen ............................................. 79

### Chapter Five
CHAPTER FIVE
Simple Polyatomic Molecules ........................................ 87
4.1. Introduction ................................................... 87
4.2. Ammonia ....................................................... 87
4.3. Phosphine ...................................................... 92
4.4. Ethylene ....................................................... 96

### Chapter Six
CHAPTER SIX
Hydrogen Cyanide and Some Related Compounds .................. 102
5.1. Introduction ................................................... 102
5.2. Hydrogen Cyanide ............................................. 103
5.3. Dicyanogen .................................................... 105
5.4. Acetonitrile ................................................... 109
5.5. Cyanogen Bromide and Cyanogen Iodide ....................... 110

### Chapter Seven
CHAPTER SEVEN
Water, Alcohols and Ethers ......................................... 120
CHAPTER EIGHT
Carbonyl Containing Compounds ................................. 148
  7.1. Introduction .............................................. 148
  7.2. Formaldehyde and Acetaldehyde ........................ 148
  7.3. Acetone .................................................. 153
  7.4. Formic Acid and Acetic Acid ............................ 155
  7.5. Discussion of the Franck-Condon Envelopes for Transitions to the Ground Ionic State .......................... 163

CHAPTER NINE
Conclusions ...................................................... 166

REFERENCES ...................................................... 167
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Correlation between the Franck-Condon Principle and the shape of UPS bands for the removal of electrons from molecular orbitals of different bonding character</td>
</tr>
<tr>
<td>2</td>
<td>Heavy particle scattering diagram using the impact parameter formulation. a. Repulsive system. b. Attractive and Repulsive system</td>
</tr>
<tr>
<td>3</td>
<td>Potential curve model showing the significance of the true $\Delta E$ energy shift. a. Repulsive Penning ionization system. b. Attractive Penning ionization system</td>
</tr>
<tr>
<td>4</td>
<td>Potential curve model showing the ratio of Penning ionization and associative ionization. a. Repulsive Penning ionization system. b. Attractive Penning ionization system</td>
</tr>
<tr>
<td>5</td>
<td>Potential curve model for ionization by a. photons and b. metastable atoms</td>
</tr>
<tr>
<td>6</td>
<td>Schematic diagram of the electron spectrometer</td>
</tr>
<tr>
<td>7</td>
<td>Schematic of the preamplifier circuit</td>
</tr>
<tr>
<td>8</td>
<td>Schematic of the control circuit</td>
</tr>
<tr>
<td>9</td>
<td>Relative transmission correction factor $T$ for the 127° electron analyzer</td>
</tr>
<tr>
<td>10</td>
<td>Background subtraction applied to the Penning electron spectrum of argon</td>
</tr>
<tr>
<td>11</td>
<td>Penning electron spectra of molecular hydrogen, deuterium hydride and molecular deuterium</td>
</tr>
<tr>
<td>12</td>
<td>Estimation of the vibrational transition probabilities for the ionization of hydrogen</td>
</tr>
<tr>
<td>13</td>
<td>Electron spectra for the ionization of molecular nitrogen</td>
</tr>
<tr>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>------</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Electron spectra for the ionization of carbon monoxide ........................................ 69</td>
</tr>
<tr>
<td>15</td>
<td>Electron spectra for the ionization of nitric oxide ............................................. 76</td>
</tr>
<tr>
<td>16</td>
<td>Electron spectra for the ionization of molecular oxygen ......................................... 80</td>
</tr>
<tr>
<td>17</td>
<td>Electron spectra for the ionization of ( \text{O}_2 ) to ( \text{O}_2^+ (X , ^2\Pi_g) ) .................................................. 81</td>
</tr>
<tr>
<td>18</td>
<td>Electron spectra for the ionization of molecular oxygen ......................................... 85</td>
</tr>
<tr>
<td>19</td>
<td>Electron spectra for the ionization of ammonia ..................................................... 89</td>
</tr>
<tr>
<td>20</td>
<td>Electron spectra for the ionization of phosphine .................................................. 93</td>
</tr>
<tr>
<td>21</td>
<td>Electron spectra for the ionization of ethylene .................................................... 97</td>
</tr>
<tr>
<td>22</td>
<td>Electron spectra for the ionization of ethylene to the ground state ion (( \bar{\text{X}}^2\text{B}_{3u} )) .................. 100</td>
</tr>
<tr>
<td>23</td>
<td>Electron spectra for the ionization of hydrogen cyanide. a. full spectra b. first band including 584 Å calibration ............... 104</td>
</tr>
<tr>
<td>24</td>
<td>Electron spectra for the ionization of dicyanogen ................................................ 107</td>
</tr>
<tr>
<td>25</td>
<td>Electron spectra for the ionization of acetonitrile ................................................ 111</td>
</tr>
<tr>
<td>26</td>
<td>Electron spectra for the ionization of cyanogen bromide ........................................ 114</td>
</tr>
<tr>
<td>27</td>
<td>Electron spectra for the ionization of cyanogen iodide .......................................... 115</td>
</tr>
<tr>
<td>28</td>
<td>Electron spectra for the ionization of water ......................................................... 122</td>
</tr>
<tr>
<td>29</td>
<td>Electron spectra for the ionization of methanol .................................................... 126</td>
</tr>
<tr>
<td>Page</td>
<td>Electron spectra for the ionization of</td>
</tr>
<tr>
<td>------</td>
<td>-------------------------------------</td>
</tr>
<tr>
<td>30</td>
<td>ethanol</td>
</tr>
<tr>
<td>31</td>
<td>isopropyl alcohol</td>
</tr>
<tr>
<td>32</td>
<td>tertiary butyl alcohol</td>
</tr>
<tr>
<td>33</td>
<td>dimethyl ether</td>
</tr>
<tr>
<td>34</td>
<td>ethylene oxide</td>
</tr>
<tr>
<td>35</td>
<td>diethyl ether</td>
</tr>
<tr>
<td>36</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>37</td>
<td>1,4 dioxane</td>
</tr>
<tr>
<td>38</td>
<td>ground ionic states of water, alcohols, and ethers. Energy shifts are given in eV</td>
</tr>
<tr>
<td>39</td>
<td>formaldehyde</td>
</tr>
<tr>
<td>40</td>
<td>acetaldehyde</td>
</tr>
<tr>
<td>41</td>
<td>acetone</td>
</tr>
<tr>
<td>42</td>
<td>formic acid</td>
</tr>
<tr>
<td>43</td>
<td>acetic acid</td>
</tr>
<tr>
<td>44</td>
<td>ground ionic state of some carbonyl containing compounds. Energy shifts are given in eV</td>
</tr>
</tbody>
</table>
**LIST OF PLATES**

<table>
<thead>
<tr>
<th>Plate</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The spectrometer</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>Complete experimental arrangement</td>
<td>49</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table | Page
--- | ---
1 | Optical selection rules in atomic spectra .......... 9
2 | $\Delta E_{\text{obs}}$ energy shifts in eV for the He*($2^1S,2^3S$) Penning ionization of molecular hydrogen, deuterium hydride and molecular deuterium at 300 °K ........................................ 59
3 | $\Delta E_{\text{obs}}$ energy shifts in eV for the He*($2^1S,2^3S$) Penning ionization of molecular nitrogen at 300 °K ........................................ 64
4 | Normalized relative vibrational transition probabilities for $N_2(X;\nu''=0) + N^+_2(X,A,B;\nu')$ for 584 Å photoionization and He*($2^1S,2^3S$) Penning ionization .......................... 65
5 | Normalized relative electronic state populations for 584 Å photoionization and He*($2^1S,2^3S$) Penning ionization of molecular nitrogen at 300 °K ........................................ 67
6 | $\Delta E_{\text{obs}}$ energy shifts in eV for the He*($2^1S,2^3S$) Penning ionization of carbon monoxide at 300 °K ........................................ 70
7 | Normalized relative vibrational transition probabilities for $CO(X,\nu''=0) + CO(X,A,B,\nu')$ for 584 Å photoionization and He*($2^1S,2^3S$) Penning ionization ........................................ 72
8 | Normalized relative electronic state populations for 584 Å photoionization and He*($2^1S,2^3S$) Penning ionization of carbon monoxide at 300 °K .... 73
9 | $\Delta E_{\text{obs}}$ energy shifts in eV for the He*($2^1S,2^3S$) Penning ionization of nitric oxide at 300 °K ...... 77
<table>
<thead>
<tr>
<th>Page</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Normalized relative electronic state populations for 584 Å photoionization and He*(2^3S) Penning ionization of nitric oxide at 300 °K .......................... 78</td>
</tr>
<tr>
<td>11</td>
<td>Normalized relative vibrational transition probabilities for O_2(X,v'' = 0) + O^+(X,v') for 584 Å photoionization and He*(2^3S) Penning ionization ................................. 82</td>
</tr>
<tr>
<td>12</td>
<td>ΔE_{obs} energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*(2^3S) Penning ionization of ammonia at 300 °K ................................. 91</td>
</tr>
<tr>
<td>13</td>
<td>ΔE_{obs} energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*(2^3S) Penning ionization of phosphine at 300 °K ................................. 95</td>
</tr>
<tr>
<td>14</td>
<td>ΔE_{obs} energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*(2^3S) Penning ionization of ethylene at 300 °K ................................. 99</td>
</tr>
<tr>
<td>15</td>
<td>ΔE_{obs} energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*(2^3S) Penning ionization of dicyanogen at 300 °K ................................. 108</td>
</tr>
<tr>
<td>16</td>
<td>ΔE_{obs} energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*(2^3S) Penning ionization of acetonitrile at 300 °K ................................. 112</td>
</tr>
<tr>
<td>17</td>
<td>ΔE_{obs} energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*(2^3S) Penning ionization of cyanogen bromide at 300 °K ................................. 116</td>
</tr>
<tr>
<td>18</td>
<td>ΔE_{obs} energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*(2^3S) Penning ionization of cyanogen iodide at 300 °K ................................. 118</td>
</tr>
<tr>
<td>19</td>
<td>ΔE_{obs} energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*(2^3S) Penning ionization of water at 300 °K ................................. 123</td>
</tr>
</tbody>
</table>
ΔΕ_{obs} energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*(2^3S) Penning ionization of methanol at 300 °K ........................................ 129

ΔΕ_{obs} energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*(2^3S) Penning ionization of ethanol at 300 °K ........................................ 130

ΔΕ_{obs} energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*(2^3S) Penning ionization of dimethyl ether at 300 °K ........................................ 138

ΔΕ_{obs} energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*(2^3S) Penning ionization of ethylene oxide at 300 °K ........................................ 139

ΔΕ_{obs} energy shift in eV for He*(2^3S) Penning ionization of diethyl ether, tetrahydrofuran and 1,4 dioxane at 300 °K ........................................ 144

ΔΕ_{obs} energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*(2^3S) Penning ionization of formaldehyde at 300 °K ........................................ 152

ΔΕ_{obs} energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*(2^3S) Penning ionization of acetaldehyde at 300 °K ........................................ 154

ΔΕ_{obs} energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*(2^3S) Penning ionization of acetone at 300 °K ........................................ 157

ΔΕ_{obs} energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*(2^3S) Penning ionization of formic acid at 300 °K ........................................ 161

ΔΕ_{obs} energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*(2^3S) Penning ionization of acetic acid at 300 °K ........................................ 162
ACKNOWLEDGEMENTS

I would like to thank sincerely Dr. C.E. Brion for his continued guidance and support throughout the course of this work. I would also like to thank my many colleagues, Mr. T. Chau, Dr. A. Hamnett, Mr. A.P. Hitchcock, Dr. S.T. Hood, Dr. S.-T. Lee, Dr. W. Stoll, Dr. W.-C. Tam and Dr. G.R. Wight for their helpful discussions and unselfish assistance on many occasions.

For the modifications and the many repairs to the apparatus, I would like to acknowledge the very capable staffs of the Electronic and Mechanical Workshops.

I thank the National Research Council of Canada for financial support and I gratefully acknowledge the receipt of an H.R. MacMillan Family Fellowship.

Finally, I would like to thank my late father, my mother and my sisters for their patience which I must have tested often, and my wife for her understanding and love.
CHAPTER ONE
INTRODUCTION

1.1. Chemi-ionization Reactions

The word chemi-ionization, first coined by Calcote, has been defined by Berry as including "all processes that result in the formation of free charges, electrons or ions, under conditions of chemical reactions". This broad definition includes ionization processes involving heavy particles colliding at thermal energies with electronically excited particles, with natural lifetimes which are comparable to the mean collision times. For the binary system (X*,A) where X* is an atom which is in a long-lived excited state and A is a target atom which is in the ground state, there are three chemi-ionization processes which may occur when the excitation potential of the excited atom X, E(X*), is greater than the ionization potential of the target atom A, IP(A).

\[ X^* + A \rightarrow X + A^+ + e \]
Penning Ionization (1.1.1.1)

\[ X^* + A + XA^{n+} + ne \]
Multiple Penning Ionization (1.1.1.2)

\[ X^* + A \rightarrow XA^+ + e \]
Associative Ionization (1.1.2)
In 1927 Penning\(^3\) demonstrated that reaction 1.1.1.1 was responsible for the lowering of the ignition voltages of neon and argon glow discharges when very small amounts of impurity gases were added. This reaction is generally referred to as Penning ionization, however, in radiation chemistry it is referred to as Jesse ionization\(^*\). Double Penning ionization has recently been reported\(^5\). Studies up to recent times of these three chemi-ionization processes have been reviewed by a number of authors\(^2,6,7\).

For the binary system \((X^*, AB)\) where \(X^*\) is an atom which is in a long-lived excited state and \(AB\) is the target molecule which is in the ground state, there are two additional chemi-ionization processes which may occur when \(E(X^*) > IP(AB)\).

\[
\begin{align*}
X^* + AB &\rightarrow X + A^+ + B + e \\
&\quad + X + A + B^+ + e \\
X^* + AB &\rightarrow XA + B + e \\
&\quad + XB^+ + A + e
\end{align*}
\]

The products of these five chemi-ionization processes may also be formed by competing autoionization processes when there are
excited states of the target particle which are resonant with $X^*$. Lampe has documented the existing work on dissociative Penning ionization and dissociative associative ionization.

1.2. Experimental Methods for Chemi-ionization Studies.

To study chemi-ionization processes, either the ions or the electrons of the exit channel may be analyzed by a number of methods.

1.2.1. Analysis of the Ions.

Five techniques have been used to analyze the ions formed in chemi-ionization processes. The first technique to be discussed is total ion collection which measures the total ionization cross-section, the parameter which links the collision dynamics and the total ionization probability. The evaluation of the total ionization cross-sections involves the rather difficult task of determining the absolute flux of the metastables which appears to have been solved only recently by Stebbings et al. Though the ionization cross-section parameter provides a meeting ground for experiment and theory, it contains relatively little information on the details of the reaction. For example, there have been a number of total cross-section calculations for the system He*(2\(^3\)S) + H, and even though different functions for the potential energy curves and the transition probability were used, they obtained rather similar answers.
The second technique used to analyze the product ions involves the use of a mass spectrometer to measure the partial cross-sections for the various chemi-ionization reactions. In the early work on chemi-ionization, mass analysis was not used and as a result, all of the ionization was attributed to Penning ionization. The extent to which the other chemi-ionization processes could compete was not known. The mass spectroscopic data up to 1969 for these chemi-ionization processes have been tabulated by Lampe. It appears that Penning ionization is the predominant process, however, in some cases, both associative ionization and dissociative associative ionization may occur to a significant extent. Using the mass spectroscopic time of flight technique, several groups have measured the velocity dependence for the partial ionization cross-sections for Penning ionization and associative ionization. Such data are of practical importance, as for example in discharge and plasma physics where partial cross-sections at high temperatures are desired. Using a simple classical version of the theoretical formulation of Penning ionization, both Illenberger and Niehaus and Pesnelle et al. independently were able to describe the measured velocity dependence of the ionization cross-section. Similar calculations have been performed by Olson.

The next two techniques to be discussed are the analysis of the energy distribution and the angular distribution of the ions produced in chemi-ionization processes. These
experiments are difficult since the ions have near thermal energies. A few attempts have been made to measure the energy distribution of ions produced in Penning ionization$^{28-30}$. Recently, Leu and Siska$^{31,32}$ have reported the measuring of the angular distribution of Penning ions of Ar, H$_2$, N$_2$, CO and O$_2$.

Finally, the technique of optical emission spectroscopy can be used to analyze the excited states of the ions produced in the chemi-ionization processes. Using a flow system where metastables collide with target particles, the afterglow which occurs when an electric discharge (used to produce the metastables) has been turned off, is optically monitored. The population of the electronic, vibrational and rotational states of the Penning ions can be determined with this method.

Schmeltekopf et al.$^{33}$ have observed the emission in a helium flowing afterglow for the transition $N_2^+(\bar{B}^2\Sigma^+_u) \rightarrow N_2^+(\bar{X}^2\Sigma^+_g)$. They have concluded that the vibrational population of the $N_2^+(\bar{B}^2\Sigma^+_u)$ is in accordance with the Franck-Condon factors for photoionization of the ground state molecule. This is a rather surprising observation as the close proximity of the helium particle at the time of ionization might well be expected to perturb the nuclear motion of the molecule. Differences have been observed in the Franck-Condon factors for $O_2^+(\bar{A}^2\Pi_u)$, HCl$^+(\bar{A}^2\Sigma^+)$ and HBr$^+(\bar{A}^2\Sigma^+)$ states formed by He*(2$^3$S) Penning ionization when compared to 584 Å photoionization$^{34,35}$. 
1.2.2. Analysis of the Electrons.

Three techniques have been used to analyze the electrons ejected in chemi-ionization processes. The first technique is the analysis of the energy distribution of the electrons. This technique is probably the most important experimental method which has been applied to the study of chemi-ionization. Since the electron is ejected in the chemi-ionization process when the metastable and the target particle are in close proximity, the electron energy distribution will contain valuable information on the reaction mechanism. The four groups which have published such experimental data are Čermák et al.\textsuperscript{36-39}, Hotop and Niehaus\textsuperscript{40-48}, Brion et al.\textsuperscript{49-56} and Coleman et al.\textsuperscript{57}. All of the electron spectroscopic studies to date indicate that Penning ionization is the predominant exit channel. Using this technique, direct information on the population of the different vibrational and electronic states of the Penning ions can be obtained.

The second technique, which is just being explored, is the analysis of the electron angular distributions measured with respect to the vector of the relative velocity of the colliding particles\textsuperscript{58,59}. In some cases, the experimental data are strongly anisotropic and asymmetric. These data provide fine details on either the transition probability matrix or the collision dynamics of Penning ionization.

The final technique to be considered is the analysis of
the spin polarization of the electrons ejected in Penning ionization with optically pumped, spin-polarized He*(2^3S) metastables. Penning ionization of He*(2^3S), Cd, Sr and Zn with He*(2^3S) metastables^60,^61 quantitatively obeys the Wigner spin rule (the total spin must be conserved in the reaction).

1.3. Excited Atoms and Molecules.

1.3.1. Introduction

When energy has been added to an atom or molecule X, as for example by absorption of a photon with a frequency \( \nu_0 \), an electron in a low-lying orbital can be promoted to a higher unoccupied orbital to produce an excited species \( X^* \).

\[
X + h\nu_0 \rightarrow X^* \tag{1.3.1.1}
\]

Some of these excited species \( X^* \) will pass spontaneously to lower states by an electric dipole transition and will emit photons. Such "optically allowed" states have lifetimes of the order of \( 10^{-9} \) seconds and therefore play a very small role in chemi-ionization processes. An example of an optically accessible state is the \( 2^1P \) state of helium which has a lifetime^62 of \( 0.56 \times 10^{-9} \) seconds.

Excited states with extremely long lifetimes were first observed many years ago. Muschlitz^63 has arbitrarily defined such an excited state to be a metastable if it's lifetime for
monomolecular decay is greater than one microsecond. One of the more important regions where metastables play an important role is in the upper and stellar atmospheres where the particle density is low and bimolecular collisions are relatively infrequent. Metastables may also play an important role in flames, electrical discharges, and plasmas. One practical application of helium metastables is in a helium/cadmium dc discharge\textsuperscript{64,65}. It appears that reactions of cadmium with He*(2\textsuperscript{3}S) metastables cause the 5 \textsuperscript{2}D states to be overpopulated with respect to the 5 \textsuperscript{2}P states resulting in strong laser action at 441.6 nm and 325.0 nm. A second practical application of metastables is that optically pumped spin-polarized He*(2\textsuperscript{3}S) metastables may provide a high flux source of polarized electrons. Keliher et al.\textsuperscript{66} have been able to extract 10\textsuperscript{-7} A electron current with up to 31% spin polarization.

The most important class of metastable is the one whose electric dipole matrix elements for transitions to all lower states are zero (or very small). These "optically forbidden" transitions can be determined by selection rules governing orbital angular momentum and electron spin. Table 1 as taken from Garstang\textsuperscript{67} lists the selection rules for electric dipole, magnetic dipole and electric quadrupole transitions for atoms. Two examples in this class of metastable are the 2\textsuperscript{1}S and 2\textsuperscript{3}S states of helium which have the respective lifetimes\textsuperscript{68,69} of 2 \times 10^{-2} seconds and 6 \times 10^{5} seconds.
TABLE 1

Optical Selection Rules in Atomic Spectra

<table>
<thead>
<tr>
<th>Electric dipole</th>
<th>Magnetic dipole</th>
<th>Electric quadrupole</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta J = 0, \pm 1$</td>
<td>$\Delta J = 0, \pm 1$</td>
<td>$\Delta J = 0, \pm 1, \pm 2$</td>
</tr>
<tr>
<td>$(0 \leftrightarrow 0)$</td>
<td>$(0 \leftrightarrow 0)$</td>
<td>$(0 \leftrightarrow 0, \frac{1}{2} \leftrightarrow \frac{1}{2}, 0 \leftrightarrow 1)$</td>
</tr>
<tr>
<td>$\Delta M = 0, \pm 1$</td>
<td>$\Delta M = 0, \pm 1$</td>
<td>$\Delta M = 0, \pm 1, \pm 2$</td>
</tr>
<tr>
<td>Parity change</td>
<td>No parity change</td>
<td>No parity change</td>
</tr>
<tr>
<td>One electron jump</td>
<td>No electron jump</td>
<td>One or no electron jump</td>
</tr>
<tr>
<td>$\Delta l = \pm 1$</td>
<td>$\Delta l = 0$</td>
<td>$\Delta l = 0, \pm 2$</td>
</tr>
<tr>
<td>$\Delta n = 0$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta S = 0$</td>
<td>$\Delta S = 0$</td>
<td>$\Delta S = 0$</td>
</tr>
<tr>
<td>$\Delta L = 0, \pm 1$</td>
<td>$\Delta L = 0$</td>
<td>$\Delta L = 0, \pm 1, \pm 2$</td>
</tr>
<tr>
<td>$(0 \leftrightarrow 0)$</td>
<td></td>
<td>$(0 \leftrightarrow 0, 0 \leftrightarrow 1)$</td>
</tr>
</tbody>
</table>
A second class of metastable is one where the outermost electron is in a Rydberg state with a very large principal quantum number. Although electric dipole transitions are allowed, the coupling of the electron and the nucleus is so weak that the probability of decay is small. For an electron of an atom with a principal quantum number $n = 30$, the mean lifetime (averaged over all angular momentum substates) is about 0.02 seconds, the ionization potential is 0.015 eV, and the orbital radius is $476 \text{ Å}$. Hotop and Niehaus have pointed out that the radiative lifetimes of Rydberg states increase with principal quantum number $n$ as $n^{5.5}$. Except for the work of Hotop and Niehaus little work has been done on such states until recently.

The properties of electronically excited particles may be quite different from those of the ground state. The principal feature of the excited species is that they have very large radii in comparison to their ground states. For excited molecules, in addition to changes in internuclear distances, geometries may also change. Finally, atomic and molecular properties of excited states such as the polarizability (which is a measure of the extent of distortion of the electron distribution in an electric field) and the dipole moment will exhibit quite different values from the ground states. For example, the single outer $2s$ electron of the He$^+(2^1S)$ metastable gives this excited species properties similar to those of lithium ($1s^2 2s$).
There are many atoms and molecules which have meta-stable states and some of these have been listed by Rundel and Stebbings\textsuperscript{70}. There is a wide variation in both the lifetimes and the excitation energies of the metastable states. The lifetimes of metastables range from as large as $6 \times 10^5$ seconds for He$^*$(2$^3$S) metastables to less than $2 \times 10^{-6}$ seconds for NO$^*$(A $^2r^+$) metastables. The excitation energies of the metastables range from as large as 56 eV for Li$^*$(4$^2P_5$) metastables to less than 1 eV for O$_2^*$(a $^1\Delta_g$) metastables.

1.3.2. Production and Quenching of Metastables.

In general, metastables may be produced by particle excitation in gaseous systems. The various methods of production of metastables have been reviewed by Stedman and Setser\textsuperscript{73}. Thermal metastables are most readily produced by electron impact excitation of the parent atom or molecule. High intensities of metastables may be produced by this method but many metastable species may be present in the beam together with photons. For the case of electron impact excitation of helium, both He$^*$(2$^1$S) and He$^*$(2$^3$S) metastable species will be present, in addition to He I (584 Å) photons. Fast metastables may be produced by charge exchange\textsuperscript{57} or by corona discharge\textsuperscript{74}.

In addition to colliding with target particles and walls, there are at least five other processes which may quench metastables. The discussion of the quenching processes will be
limited to the species He*(2^1S) and He*(2^3S).

The single photon decay of the He*(2^1S) metastable is strictly forbidden and the process which probably governs its lifetime is the spontaneous double photon radiative decay.

\[
\text{He}^*(2^1\text{S}) + \text{He}^*(2^1\text{S}) \rightarrow \text{He}^*(1^1\text{S}) + \gamma_1 + \gamma_2
\]

(1.3.2.1)

where two photons of frequencies \( \gamma_1 \) and \( \gamma_2 \) are emitted. It is only necessary that the energies of the two emitted photons satisfy the energy conservation requirement

\[
\gamma_1 + \gamma_2 = 20.615 \text{ eV}
\]

(1.3.2.2)

which is the excitation potential of the He*(2^1S) metastable. The single photon decay of helium in the 2^3S state though not strictly forbidden, is highly improbable and decay appears to occur preferentially by two-photon emission\(^75\).

The He*(2^1S) metastable has been routinely quenched\(^3,76\) with the unfiltered light of a helium lamp. The resonant \( (2^1\text{S}_0 - 2^1\text{P}_1) \) 20,587 Å radiation excites the 2^1S\( _0 \) state to the 2^1P\( _1 \) state which can then decay to the ground 1^1S\( _0 \) state with the emission of 584 Å photons. It is possible to quench over 99% of the helium singlet metastables using this optical pumping technique. The He*(2^3S) metastables cannot be coupled to the ground state by this method.

The He*(2^1S) metastables also may be quenched by electron impact. Quenching may then occur by excitation to a
neighbouring radiative state which is similar to the previously discussed quenching process. Quenching may also occur as a result of direct superelastic electron exchange.

\[ \text{e} + \text{He}^*(2^1S) \rightarrow \text{e} + \text{He}^*(2^3S) + 0.79 \text{ eV} \quad (1.3.2.3) \]

With thermal electrons, the cross-section for this process is large\(^{77}\) and thus He\(^*(2^1S)\) is effectively converted to He\(^*(2^3S)\).

A dc electric field may be used to quench the He\(^*(2^1S)\) metastable by coupling it to an excited state which can radiate to the ground state. The large separation (0.6 eV) of the \(2^1S_0\) level from the closest radiating \(2^1P_1\) state requires the application of a field of \(2 \times 10^5 \) V/cm to achieve 90% quenching\(^{78}\).

Finally, metastables may be quenched by an excitation transfer process. If this process is to occur with a significant probability, there must be an energy level of an excited state of the target particle AB** which is resonant with the excitation energy of the metastable. A well known example of an excitation transfer process is

\[ \text{He}^* + \text{Ne} \rightarrow \text{He} + \text{Ne}^{**} \quad (1.3.2.4) \]

which occurs in helium/neon lasers. Difficulties will arise in the interpretation of Penning electron spectra if the excited state of the target particle can autoionize. Complications will arise if the excited state dissociates to yield excited fragments which autoionize. These problems are analogous to the competing autoionization processes which may occur in photoionization.
CHAPTER TWO

IONIZATION PROCESSES

2.1. Photoionization

2.1.1. Introduction

In 1905 Einstein\textsuperscript{79} postulated the photoelectric effect which states, when an atom or molecule interacts with a photon of frequency $v_1$ which has sufficient energy to eject an electron, ionization will occur.

$$h v_1 + AB + AB^+ + e$$  \hspace{1cm} (2.1.1.1)

Any excess energy will manifest itself as kinetic energy which will be partitioned between the two particles formed. Because of the large difference in mass between the ion and the ejected electron and through consideration of the conservation of momentum, virtually all of the excess kinetic energy $E'_e$ will be carried away by the photoelectron. By utilizing the Einstein photoelectric equation

$$E_b = h v_i - E'_e$$  \hspace{1cm} (2.1.1.2)

the binding energy $E_b$ of electrons in atoms or molecules can be evaluated by measuring the kinetic energy of the photo-ejected electrons. Equation (2.1.1.2) can be written in a more familiar form

$$E'_e = h v_i - IP^a(AB) - E^+(v')$$  \hspace{1cm} (2.1.1.3)

where $IP^a(AB)$ is the adiabatic ionization potential which is the
difference in electronic energy between the lowest vibrational levels of the ion and the molecule, and $E^+(v')$ is the vibrational energy of the $v'$ level of the ion.

The experimental technique which measures the kinetic energies of photoelectrons is referred to as photoelectron spectroscopy and in the last ten years it has become a routine tool for studies in molecular spectroscopy. In photoelectron spectroscopy the photon source must be monochromatic, and it must have a usable intensity. To analyze inner or core shell electrons, high energy X-ray sources such as Al K$_\alpha$(1486.6 eV) are used and this technique is commonly referred to as Electron Spectroscopy for Chemical Analysis (ESCA)\textsuperscript{80} or X-ray Photoelectron Spectroscopy (XPS). To analyze outer or valence shell electrons, the most popular photon source has been the He I resonance line at 584 Å (21.217 eV) and this technique is commonly referred to as UV Photoelectron Spectroscopy (UPS). Both methods have recently been reviewed by Lee\textsuperscript{81}. This thesis is concerned with the study of valence shell electrons, thus discussions related to photoionization will be restricted to the regime of UPS.

2.1.2. Franck-Condon Principle.

Photoionization of a diatomic molecule can be described as a vertical or Franck-Condon transition between two molecular potential curves. This is a consequence of the Born-Oppenheimer approximation\textsuperscript{82} which states that the relative position and velocity of the nuclei may be assumed to be unchanged for electronic
transitions that take place in a time interval which is much shorter than that required for a single vibration. In Figure 1 a Franck-Condon transition for the photoionization of a diatomic molecule may be viewed as a vertical transition between the potential curves of the ground state molecule and an ionic state. The region in which vertical transitions occur with some finite probability is frequently called the Franck-Condon region and is indicated by the shaded region on Figure 1.

Vibrational structure is often observed when molecules are photoionized. The vibrational intensities may be quantitatively described by the wave mechanical description of the Franck-Condon principle. The intensity of a vibrational peak in an electronically allowed transition is proportional to the absolute square of the overlap integral

\[ I_{v', v''} \propto \left| \int \psi_{v'}^\ast \psi_{v''} \, dQ \right|^2 \]  

(2.1.2.1)

where \( \psi_{v'} \) and \( \psi_{v''} \) are the vibrational wavefunctions of the upper and lower quantum states and \( Q \) is the nuclear co-ordinate. The Franck-Condon factor will be significant when the maxima or minima of the two wave functions lie directly above each other. For \( \psi_{v=0} \), the maxima of the wavefunction occurs at the equilibrium internuclear distance of the molecule, however for \( \psi_{v>0} \), the maxima or minima occurs near the classical turning points of motion.

The photoelectron energy distribution of an ionic state
FIGURE 1. Correlation between the Franck-Condon Principle and the shape of UPS bands for the removal of electrons from molecular orbitals of different bonding character.
of a diatomic molecule depends on the shape and position of the potential curve of the resulting ion. If for example, an electron is removed from an antibonding orbital, the equilibrium internuclear distance of the ion will be smaller than that for the molecule. Thus, the slow rising attractive portion of the potential curve of the ion will lie above the Franck-Condon region of the ground state neutral, and only a few vibrational levels of the ion will be populated (see Figure 1). This suggests that from the intensity and the number of vibrational levels observed in the photoelectron data, it may be possible to extract information on the nature of the molecular orbital from which the electron was ejected. Illustrated in Figure 1 is a number of electron energy distributions which result when an electron is removed from various types of molecular orbitals.

It is possible to understand polyatomic molecules by extending the principles applied to diatomic molecules. The situation is now very complicated as transitions occur between multidimensional surfaces. Analysis of the vibrational structure may be difficult as several vibrational modes may be excited simultaneously.

2.1.3. Autoionization

In the photoionization process it is possible to remove an electron from an atom or molecule by a process which does not
involve a direct transition into the ionization continuum. This process is known as autoionization which may be regarded as a two step process. First, the initial excitation of an electron occurs into a discrete state above the ionization potential of the species. This discrete state must have an energy level which is resonant with the excitation energy of the photon. The second step of the process involves a radiationless transition from the discrete state into the accessible ionization continuum.

Distortion of the Franck-Condon factors for the photoionization of a molecule may be the result of a competing autoionization process. Anomalous Franck-Condon factors for the ground state ion of oxygen resulting from photoionization with Ne(736,744 Å) radiation have been explained by such a process. 85

2.2. Penning Ionization.

2.2.1. Qualitative Description

For Penning and associative ionization at thermal energies

\[ X^* + AB \rightarrow X + AB^+ + e \]  \hspace{1cm} (2.2.1.1)

\[ \rightarrow XAB^+ \]  \hspace{1cm} (2.2.1.2)

the motion of the heavy particles can be described adequately using classical theory. Figure 2 shows two scattering events during which both attractive and/or repulsive forces act. At large distances (beyond the range of figure 2) the weak van der Waals
FIGURE 2. Heavy particle scattering diagram using the impact parameter formulation. 

(a) Repulsive system.

(b) Attractive and Repulsive system.
attractive forces are predominant and in both cases the metastable particle approaches the target species A or B. In Figure 2.a, the trajectories for two different impact parameters illustrates that the metastable particle only sees a repulsive potential. In Figure 2.b, for the case with the relatively large impact parameter $\rho_1$, the metastable particle sees only an attractive potential, but for the case with the relatively small impact parameter $\rho_2$, the metastable particle first sees an attractive potential and after penetrating to the repulsive part of the potential, it is repelled at the classical turning point. In Figure 2, $R_o$ is the closest distance of approach for the various impact parameters of the two scattering events and it is at this point where there is the greatest probability that the energy contained in the metastable will be transferred to the target particle.

Though the actual energy exchange mechanism for Penning ionization is unknown, there is evidence that electron exchange, as proposed by Hotop and Niehaus$^{41,43}$, occurs. The Hotop-Niehaus model, based on theory used to explain the Auger deexcitation of an excited atom at a metal surface$^{86}$, may be described by the process

$$X^*(1) + A(2) \rightarrow X(2) + A^+ + e (1) \quad (2.2.1.3)$$

where $X^*(1)$ represents a metastable with an excited electron (1) and $A(2)$ is a ground state target particle with a valence electron (2). The transition process in Penning ionization can
be viewed as a tunnelling of electron (2) to the vacant ground state orbital of the metastable, followed by Auger emission of electron (1). Preliminary studies by Keliher et al.\textsuperscript{67} of the electron spin polarization for Penning ionization support the electron exchange mechanism if the Wigner spin rule is obeyed\textsuperscript{60,61}.

2.2.2. Potential Curve Model

Penning ionization is a problem involving heavy particle inelastic collisions and in principle it can be treated by using a potential curve model. This model was first applied to Penning ionization by Herman and Čermák\textsuperscript{28,88} and was later developed by Hotop and Niehaus\textsuperscript{41,42,44}.

For low energy (thermal) collisions and within the Born-Oppenheimer approximation for the separation of electronic and nuclear motion, the potential curve model for the system (X*,A) is illustrated in Figure 3. The incoming channel (X*,A) is assigned a Born-Oppenheimer like potential V*(R) which is a function of the internuclear distance R between the metastable and the target atom (and should not be confused with the potential curves of the diatomic molecule which were discussed in section 2.1.2.). In Figure 3.a, V*(R) is shown as a purely repulsive potential which corresponds to the scattering events shown in Figure 2.a. In Figure 3.b, V*(R) is shown to contain both an attractive and a repulsive potential which corresponds to the scattering events shown in Figure 2.b. Also shown is the
FIGURE 3. Potential curve model showing the significance of the true ΔE energy shift. a. Repulsive Penning ionization system. b. Attractive Penning ionization system.
potential $V^+(R)$ for the outgoing system $(X,A^+,e)$. Thus, for all separations $R$, $V^*(R)$ is a discrete state which is embedded in $V^+(R)$, the continuum of states to which it is coupled. The two particles $(X^*,A)$ enter along the curve $V^*(R)$ with some kinetic energy $E_k$. At any point along this curve there is a definite probability $W(R)$ that a vertical transition to $V^+(R)$ will occur. The energy of the ejected electron at that point will be

$$E_{el}(R) = V^*(R) - V^+(R)$$

(2.2.2.1)

as indicated in Figure 3 by the third curve which represents the difference between $V^*(R)$ and $V^+(R)$. For transitions at large $R$ ($R \gg 10 \AA$) the energy of the ejected electron will be equal to $E_{el}^0$, the nominal energy for the ionization process.

$$E_{el}(R \to \infty) = E(X^*) - IP(A)$$

(2.2.2.2)

$$= E_{el}^0$$

(2.2.2.3)

At smaller $R$, the energy of the ejected electron will be different from $E_{el}^0$ in a way which is characteristic of the two potential curves $V^*(R)$ and $V^+(R)$. The transition probably $W(R)$ determines the internuclear range where a transition will occur with significant probability and this will strongly influence the shape of the electron energy distribution.

Within the framework of classical mechanics it is possible to estimate the shape of electron energy distributions by assuming that the transition probability $W(R)$ is largest at the classical turning point and decreases exponentially with
increasing $R$. For the repulsive Penning ionization system (Figure 3.a), $E_{e1}^0$ will be the lower boundary of the electron energy distribution for transitions occurring at large $R$ ($R >> 10$ Å) regardless of the kinetic energy between the two particles. The upper boundary of the electron energy distribution is dependent on the relative kinetic energy of the system. If the particles have a relative kinetic energy of $E_{k1}$ and a transition occurs at the classical turning point $R_{cl}$, the upper boundary of the energy distribution is $E_1$. Since the transition probability is largest at the classical turning point, $R_{cl}$, the electron energy distribution will have the most intense structure at the energy $E_1$. One quantity which is related to the four parameters $V^-(R)$, $V^+(R)$, $W(R)$ and $E_k$ is the energy difference between the expected nominal energy $E_{e1}^0$ and the peak maximum of the energy distribution. This parameter is known as the true energy shift, $\Delta E$, and is indicated on Figure 3.a as having a positive value. When the relative kinetic energy between the two particles is increased to $E_{k2}$, the width of the Penning electron energy distribution increases and consequently, the true $\Delta E$ energy shift value also increases.

The situation differs for the attractive Penning ionization system. The lower boundary of the energy distribution is dependent on the shape of the two potential curves and occurs for one specific transition at small $R$ ($R < 10$ Å). When the
relative kinetic energy of the two particles is small \( (E_{k1}) \), the width of the electron energy distribution is constant since the upper boundary of the electron energy distribution is the nominal energy \( E_{el}^0 \). When the relative kinetic energy of the two particles is large \( (E_{k2}) \), the width of the electron energy distribution varies since the upper boundary of the electron energy distribution is dependent on \( E_{k2}^0 \). For the portion of the electron energy distribution which is less than \( E_{el}^0 \), transitions occurring at two different internuclear separations \( R \) may contribute to the spectrum. Finally it is noted that the true \( \Delta E \) energy shift value is indicated as having either a positive or a negative value, as shown in Figure 3.b.

The quantities \( V^*(R) \), \( V^+(R) \) and \( W(R) \) are strongly coupled and in general it is not possible to derive a unique set from the electron energy distribution alone. If "a priori" knowledge of \( V^*(R) \), from detailed elastic scattering experiments was available, both \( V^+(R) \) and \( W(R) \) could be deduced from electron energy distributions.

For the special case where the depth of the potential well, \( \epsilon^* \), for \( V^*(R) \) is very much larger than depth of the potential well, \( \epsilon^+ \), for \( V^+(R) \) and the minimum of the potential well for \( V^*(R) \) occurs at a larger internuclear separation than for \( V^+(R) \), it is possible that \( \epsilon^* \) can be obtained from the electron energy distribution. Hotop and Niehaus have shown
that the measured electron energy distribution for the system (He\textsuperscript{#},Na) is consistent with this model. The potential \( V^*(R) \) was described by a Lennard-Jones (12,6) potential and the transition probability was described by a simple exponentially decreasing function

\[
W(R) = W_0 \exp(-\alpha R)
\]  

(2.2.2.4)

This function decreases in the same manner as the square of the wave function for an electron bound to an atom. By varying \( \alpha \), Hotop and Niehaus were able to make a very good fit between experiment and theory.

The ratio of the partial cross-sections for associative to Penning ionization can be estimated from the electron energy distribution, as shown on Figure 4. For the repulsive system where the relative kinetic energy is \( E_{k1}^+ \) (Figure 4.a), Penning ionization will occur at all internuclear distances \( R > R_{pi} \) such that the energy of the ejected electron

\[
E_{el1} < E_{el}^0 + E_k
\]  

(2.2.2.5)

If a transition occurs at \( R > R_{pi} \) to a point on the potential curve \( V^+(R) \) that lies within the potential well \( \epsilon^+ \), the particles will have sufficient kinetic energy to escape the well. Associative ionization will occur at all internuclear distances \( R_{ci1} < R < R_{pi} \) such that

\[
E_{el} > E_{el}^0 + E_k
\]  

(2.2.2.6)

Transitions which occur at \( R_{ci1} < R < R_{pi} \) will lie on points on the potential curve \( V^+(R) \) that are within the potential well
FIGURE 4. Potential curve model showing the ratio of Penning ionization and associative ionization. a. Repulsive Penning ionization system. b. Attractive Penning ionization system.
and the particles will have kinetic energies which are not sufficient to escape the potential well, thus associative ions XAB\(^+\) are formed. If the relative kinetic energy \(E_k\) is known, the ratio of the two ionization processes can be evaluated from the two areas under the electron energy distribution curve. It is noted that associative ionization does not occur for the specific examples of the attractive Penning ionization system illustrated in Figure 4.b.

This potential curve model may be extended in principle to polyatomic molecules with transitions occurring between multidimensional potential surfaces. An additional complication is the fact that molecules may have several vibrationally excited modes.

2.2.3. Quantum Mechanical Treatment of the Potential Curve Model.

Quite recently, a number of authors\(^8,9,48,70,89,90\) have reviewed the theoretical treatments of the Penning ionization of atoms. Penning ionization can be viewed as a reaction which depends upon the configuration interaction between a discrete molecular state which is embedded in a continuum of molecular states. Within this framework, Nakamura\(^91\) has derived a rigorous quantum mechanical formalism for this problem in which the non-adiabatic effects due to the relative motion of the particles are properly included. However, use of this formalism involves very complicated and lengthy calculations and as of yet has not been applied to any system.
For Penning ionization at thermal energies, the adiabatic approximation which neglects the influence of the relative motion, can be expected to be good. Nakamura has also developed a quantum mechanical formalism for Penning ionization in the adiabatic approximation. Fujii et al. have used this formalism in their calculations for the three electron problem

\[ \text{He}^+ + H \rightarrow \text{He} + H^+ + e \]  

(2.2.3.1)

which is the simplest possible Penning ionization process. However, in their calculations they have appeared to neglect some avoided crossings which can significantly effect the potential curve \( V^*(R) \). For example, the \( \text{He}^*(2^1S) + H \) potential curve is repulsive in the zero order approximation and it has an avoided crossing with the attractive \( \text{He}^*(2^3P) + H \) curve which makes the \( \text{He}^*(2^1S) + H \) potential attractive. Fujii et al. have calculated cross-sections which are in agreement with the experimental results reported by Shaw et al.. Errors in these calculations might be expected due to the approximations used in calculating the potential curves. Miller et al. have also used the adiabatic formalism in a theoretical treatment of Penning ionization. Using sophisticated configuration interaction calculations on the system \( \text{He}^* + H \), they obtained potential curves which were quite different from Fujii et al.. Cohen and Lane extended the work of Miller and, using both classical and semi-classical methods, they obtained ionization cross-sections which were in good agreement with experiment.
data. From the detailed calculations of Miller\textsuperscript{17,29,26} it is possible to obtain the ratio of associative to Penning ionization. The calculations suggest for the reaction between He\textsuperscript{*} + H, there should be 18% HeH\textsuperscript{+} and 82% H\textsuperscript{+} which is in rough agreement with the experimental data from flowing afterglow measurements\textsuperscript{92}.

2.2.4. Penning Electron Spectra of Molecules.

Because the physical properties of a neutral metastable at thermal energies are very different from those of a photon, the nature of the collision process for the two modes of ionization should be very different. This is reflected in the fact that both the collision duration, defined by the time required for the slowest particle to pass through a collision sphere with a diameter of one angstrom and the collision cross-section for Penning ionization (10\textsuperscript{-13} seconds, 10\textsuperscript{-16} cm\textsuperscript{2}) are very much larger than for photoionization (10\textsuperscript{-16} seconds, 10\textsuperscript{-19} cm\textsuperscript{2}).

Three general features of the Penning electron energy distribution to be discussed with respect to the analogous photoelectron energy distribution are the shapes of the vibrational envelope of an ionic state, the relative electronic state populations of the molecule and the energy shifts of the electron spectra.

a. Shape of the Vibrational Envelope.

In general, the He\textsuperscript{*}(2\textsuperscript{1}S,2\textsuperscript{3}S) Penning electron spectra are remarkably similar in appearance to their analogous 584 Å photoelectron spectra\textsuperscript{46,49-56}. Any ionic state observed in photoionization will also be observed in Penning ionization. It is noted that structure in a Penning electron
spectrum is always broader than the analogous structure in the photoelectron spectrum. The degree to which the structure is broadened in Penning ionization appears to be a function of the relative kinetic energy between the metastable and the target molecule. In favourable cases where vibrational structure for an ionic state is resolved\(^5,^{51,53}\), the vibrational spacings for the two ionization processes are the same within experimental error. In addition, the relative vibrational intensities (or the Franck-Condon factors) of an ionic state are often very similar for the two modes of ionization\(^5,^{51,53}\). This suggests that the Penning ionization process is a vertical transition, like photoionization.

There exist a number of apparently anomalous cases where the shape of the vibrational envelopes observed in Penning ionization are different from those observed in photoionization. For example, Richardson and Setser\(^3\) have observed such differences in afterglow studies which apparently are due to competing processes. A direct analysis of such an anomaly using electron spectroscopic techniques requires that vibrational structure in the Penning electron spectra be resolved. For the process \(\text{He}^+(2^3S)\text{O}_2^+(\pi^2\Pi_g)\) as studied by electron spectroscopy\(^51\), an observed anomaly has been traced to an autoionizing level of \(\text{O}_2\) which is essentially resonant with the \(\text{He}^+(2^3S)\) energy. For the Penning ionization of a number of molecules, anomalies have been observed which apparently are not due to competing autoionization processes\(^55,56\). For these cases it has been suggested that the collision between the metastable and the target molecule is
sufficiently "sticky" to distort the ground state of the target molecule along some combination of normal modes, but the ion state does not interact significantly with the neutral ground state metastable (therefore it's geometry remains effectively unaltered). This proposed type of mechanism is illustrated schematically by the potential energy curves of Figure 5. For the photoionization process, a vertical transition occurs between $M$, the normal ground state of the target and $M^+$, the final ionic state of the target. For the Penning ionization process, a vertical transition occurs between $M_x$, the ground state of the target which is perturbed by the metastable atom and $M^+$, the final ionic state of the target. The abscissa refers to any normal coordinate of the target. In this particular hypothetical case, the most intense transition is shifted from $(0'^n\rightarrow 0')$ for photoionization to $(0''\rightarrow 2')$ for Penning ionization. The shape of the vibrational envelopes for the two processes are significantly different. Calculations\textsuperscript{54} suggest that a perturbation of the target potential curve of the magnitude of 0.2 Å could account for the differences observed for the vibrational envelopes.

b. Relative Electronic State Populations.

One point where Penning ionization and photoionization generally differ is when the relative electronic state populations of the ion are compared. It may be necessary to correct the electron energy distribution with an electron analyzer transmission function, before such comparisons are made. This laboratory has studied a number of molecules\textsuperscript{49-56} and large differences in the state populations have been observed when
Figure 5. Potential curve model for ionization by a. photons and b. metastable atoms.
comparing the two modes of ionization. In a series of molecules containing \(-\text{C}=\text{N}\), the ratio of the normalized relative populations of states corresponding to the removal of \(\pi\) bonding and nitrogen lone pair electrons is significantly greater for 584 Å photoionization than for \(\text{He}^*(2^3\text{S})\) Penning ionization\(^{55}\). In general when comparing the state populations for the two modes of ionization, it is not possible to make adjustments for possible effects due to differences in excitation energies. Instead of comparing the \(\text{He}^*(2^1\text{S},2^3\text{S})\) Penning electron spectrum to the 584 Å photoelectron spectrum, ideally the \(\text{He}^*(2^1\text{S})\) Penning electron spectrum should be compared to the 601 Å (20.62 eV) photoelectron spectrum and the \(\text{He}^*(2^3\text{S})\) Penning electron spectrum should be compared to the 626 Å (19.82 eV) photoelectron spectrum. Measurements of the partial cross-sections as a function of the "photoionization" energy indicate that the relative electronic state populations of a number of molecules\(^{93-95}\) can change drastically even over a few volts. In addition, it is not possible to make adjustments for differences in the angular distribution of ejected electrons arising from different ionic states. Ideally, the electron distributions for the photoionization process should be measured at the "magic angle" of 54.7 degrees. At this angle, the electron energy distributions will be independent of the angular anisotropy parameter \(\beta\). However, it appears that at 90 degrees, the \(\beta\)-parameter produces only small variations in the relative state populations. Only a few Penning electron angular distribution studies\(^{58,59}\) have been performed to date. The angular distribution studies for the Penning ionization of argon\(^{58}\) suggest that such an effect may be relatively small.
c. Energy Shifts.

The "expected value" of the kinetic energy of the electron ejected in the Penning ionization process, $E_{el}^0$, can be derived from an expression

$$E_{el}^0 = E(X^*) - IP^a(AB) - E^+(v') \quad (c.1)$$

which is analogous to the expression (2.1.1.3) which evaluates the kinetic energy of the electrons ejected in the photoionization process. With respect to a photoelectron spectrum the corresponding "expected" Penning electron spectrum should be shifted to lower electron energies by an amount $(hv_1 - E(X))$.

In general, the "observed" Penning electron spectra are shifted to lower electron energies (with respect to their corresponding photoelectron spectra), however the magnitudes of these shifts differ from the expected amount $(hv_1 - E(X^*))$ by a value, $\Delta E_{obs}$. This value is experimentally obtained using the expression

$$\Delta E_{obs} = E_{el}^m - [E(X^*) - IP^v(AB)] \quad (c.2)$$

where $E_{el}^m$ is the observed energy of the ejected electron corresponding to the peak maximum of the state under consideration for the Penning ionization process, and $IP^v(AB)$ is the vertical ionization potential (measured by photoelectron spectroscopy) of the same state under consideration.

The $\Delta E_{obs}$ energy shift value contains a number of components and has been defined\(^5\)

$$\Delta E_{obs} = \Delta E + \Delta E_A + \Delta E_P \quad (c.3)$$

where $\Delta E$ is the true energy shift value for the Penning ionization process, $\Delta E_A$ is the shift in the peak maximum caused
by competing autoionization processes and $\Delta E_p$ is the shift in the peak maximum caused by any perturbation of the target potential curves (see Figure 5). The significance of the true $\Delta E$ energy shifts for Penning ionization has been discussed in a previous section. Experimentally this term has generally been found to be of the magnitude of thermal energies$^{51,53,55}$. Therefore, Penning ionization electron spectroscopy cannot be used as a technique to accurately determine ionization potentials of atoms and molecules. Difficulties may arise in attempting to evaluate a true $\Delta E$ energy shift value for a single state when a competing autoionization process occurs and/or in the situation where the potential energy curves of the target molecule are appreciably modified in Penning ionization. Either of these situations may alter the shape of the envelope observed for transitions to an ionic state. If the envelope shape is changed, the peak maximum for the ionic state may also change. It should be noted that $\Delta E_A$ and $\Delta E_p$ will correspond to some simple multiple of vibrational quanta. To be able to evaluate the true $\Delta E$ from $\Delta E_{\text{obs}}$, vibrational structure must be apparent in the Penning electron spectra.
CHAPTER THREE

EXPERIMENTAL

3.1. Introduction.

The study of chemi-ionization processes by analyzing the energy distribution of the ejected electrons requires an experimental configuration consisting of a metastable source, a collision chamber and an electron energy analyzer. A photon source is also desirable so that comparisons may be made between chemi-ionization and photoionization processes. The apparatus used in this work is shown schematically in Figure 6. Plate 1 is a photograph of the spectrometer. The apparatus was originally designed by Stewart but it has subsequently been modified.

3.2. The Spectrometer.

3.2.1. Metastable Source.

The metastable source consists of an excitation region where metastables are formed and a set of grids which are used to trap charged particles.

Commercial tank helium is introduced into the excitation region by means of a variable leak valve. The gas enters the excitation chamber at an angle of 45 degrees to minimize the scattering of helium due to momentum transfer from the exciting electrons. The gas enters through a fused array of
FIGURE 6. Schematic diagram of the electron spectrometer.
PLATE 1. The spectrometer.
quartz capillaries (pore diameter = 0.05 mm., thickness = 0.5 mm). Studies to determine the importance of the quartz array showed a marked improvement in the signal to noise ratios for the Penning electron spectra. This suggests that the directional properties of the helium gas flow are improved by the quartz array. The gas is then bombarded in the excitation region by electrons of variable energy. Electrons are produced from a directly heated tungsten filament (0.038 mm x 0.76 mm) and are accelerated (typically to 600 eV) through a slit into the excitation chamber. The total electron emission varies between 2 and 20 millamps depending on the source conditions. An electrically isolated water cooled copper block surrounds the excitation chamber (see Plate 1). The cooling block reduces both the ambient temperature at the collision centre from 500°K to 300°K and the time required to achieve thermal equilibrium. Any charged particles produced in the excitation chamber are confined in the metastable source by proper biasing of the ion and electron trapping grids (90% transmission). Two configurations have been used to trap the charged particles. In mode A, the electrons are the first particles to be trapped, then the ions are trapped. In mode B, the charged particle traps are reversed. The best signal to noise ratios are obtained when the traps are operated in mode A with a potential of 22.5 V to trap the electrons and a potential of 135 V to trap the ions.

3.2.2. Collision Region.

The distance from the centre of the collision region
to the centre of the excitation chamber is 7.62 cm and therefore
the only processes to be observed will involve metastables with
lifetimes greater than $6 \times 10^{-4}$ seconds. Two annular stops with
apertures of 6.35 mm and 8.89 mm have been added to the colli-
sion region. These stops have reduced the collision volume of
the original apparatus by a factor of 20 (present dimensions of
the collision chamber : length = 1.27 cm, diameter = 2.54 cm).
Studies using the stops have shown that the decrease in the
scattering of low energy secondary electrons, produced when the
metastables collide with the apparatus walls, results in a
significant reduction in the background, particularly at lower
electron energies.

3.2.3. Electron Analyzer.

The kinetic energies of electrons ejected in chemi-
ionization processes may be measured by the deflection of the
electrons in an electric and/or magnetic field. The properties
and the relative merits of various types of electron energy
analyzers have been discussed in a number of review articles$^{96-99}$.

The electrostatic analyzer has a number of properties
which makes it suitable for studying chemi-ionization processes.
Generally speaking, electrostatic fields are easier to produce
and regulate than magnetic fields. In addition, it is relatively
easy to eliminate fringing fields. When an electrostatic
analyzer of the deflection type is used, a differential spectrum
is obtained. This has an advantage in that accurate assignments
of energy levels are possible. A 127 degree electrostatic analyzer was preferred over a 180 degree electrostatic analyzer because it is relatively easy to construct and it is less susceptible to spurious magnetic fields. Finally, the use of slit geometry in the 127 degree analyzer permits a sampling of a relatively large area.

The 127 degree electron analyzer used in this study was constructed from brass components which are spaced and located by precision sapphire balls. The analyzer plates are coated with benzene soot to form a homogenous conducting surface that minimizes scattering of low energy secondary electrons.

From first principles, Tam\textsuperscript{100} has discussed the theory of the 127 degree analyzer. The analyzing energy of the electron, $E_a$, within the analyzer, can be evaluated from the expression

$$V_{ab} = 2E_a \ln \left( \frac{b}{a} \right)$$

(3.2.3.1)

where $V_{ab}$ is the potential difference between the analyzer plates, $b$ is the outer radius of the analyzer, and $a$ is the inner radius of the analyzer. The value of these parameters in the present case are: $V_{ab} = 1.0$ eV, $b = 27.5$ mm and $a = 22.5$ mm. Thus, under typical conditions, the pass energy of the analyzer has been calculated to be 2.52 eV. The resolution of the 127 degree analyzer including angular effects has been evaluated from the expression\textsuperscript{100}
\[
\frac{\Delta E}{E_a} = \frac{W}{r_0} + \frac{\alpha}{3}
\]

where \(\Delta E\) is the full width at half maximum (FWHM) of the
electron energy distribution, \(W\) is the width of the exit slit,
\(r_0\) is the mean radius of the electron analyzer and \(\alpha\) is the
half angle of acceptance. The values of these parameters are:
\(W = 0.4 \text{ mm}, r_0 = 25.0 \text{ mm}, \) the half angle of acceptance of the
electrons produced by an external photon source \(\alpha_{ph} = 2^o\) and
the half angle of acceptance of the electrons produced by
metastables† \(\alpha_{He^*} = 6^o\). Thus, for photoionization, the FWHM
is calculated to be 0.044 eV. This can be compared to an
experimental value of 0.048 eV FWHM on the \(\text{Ar}^+(2P_3/2)\) peak. For
Penning ionization, the resolution is calculated to be 0.044 eV.
Folding the natural width\(^{b2}\) of 0.035 eV for the process
\(\text{He}^*(2S)\text{Ar}^+(2P_3/2)\) into the observed instrumental resolution
results in a calculated FWHM of 0.091 eV which is in good agree­
ment with the observed value of 0.097 eV.

The analyzer is operated in a constant resolution mode,
that is, \(V_{ab}\) is kept constant during a scan. The scanning vol­
tage is applied between the collision chamber which is at ground
potential, and the entrance slit of the analyzer. This voltage
is obtained from the amplification of a four volt ramp which
originates from the multichannel analyzer in which the spectrum
is accumulated.

† the value of \(\alpha_{He^*} = 8^o\) quoted in Reference 50 was
calculated from a relationship\(^{37}\) which evaluates
the resolution of a 127 degree electron analyzer
incorrectly.
Inside the vacuum system, an un-annealed mu-metal shield surrounds both the electron analyzer and the collision region. Within the shield there exists a homogenous magnetic field of 100 milligauss. This shield is very effective in reducing any stray magnetic fields due to external interference.

3.2.4. Electron Detection.

The electrons which pass through the analyzer are collected by a closed-end channel electron multiplier (Mullard B419AL). The 8 mm entrance cone of the multiplier and the output are biased respectively with voltages of +90 V and +2.4k V with respect to ground potential. Since only relative cross-sections are measured, the actual value of the efficiency of the multiplier is unimportant and no calibration has been made. The electron multiplier is well shielded to exclude spurious electron currents. The counting equipment is conventional and is comprised of a preamplifier (see Figure 7), an amplifier and a discriminator. A chart recorder, ratemeter or multichannel analyzer may be used as output devices.

Figure 8 is a schematic diagram of the control circuit.

3.2.5. Light Source.

The external light source is a low pressure 2450 MHz microwave discharge in helium. The microwave cavity was constructed from brass and has been described by Brion\textsuperscript{101}. Samson\textsuperscript{102} has reported the characteristics of such a source. The most
FIGURE 7. Schematic of the preamplifier circuit.
FIGURE 8. Schematic of the control circuit.
intense line is the 584Å He I resonance line. This line arises from the $2^1P + 1^1S$ resonance transition in helium and has sufficient energy to ionize all gases except for helium and neon.

3.2.6. Vacuum System.

A picture of the complete experimental arrangement is shown in Plate 2. The vacuum system consists of three regions, the sample handling region, the spectrometer chamber and the light source region, and is essentially the same as described by Stewart.

The sample handling region consists of two inlets which are coupled to a common variable leak valve (Granville-Phillips 203) which leads into the spectrometer. One system, for corrosive gases and organic chemicals, is constructed entirely of stainless steel while the other, for non-corrosive gases, is constructed of brass and utilizes teflon seals.

The main spectrometer chamber was constructed from stainless steel with Viton O-rings providing the vacuum seal. Electrical connections were made via ceramic octal-seals or single feed-throughs. The vacuum was maintained by two NRC 8" diffusion pumps (using Convalex -10, a polyphenyl ether) with liquid nitrogen cold traps and water baffles, each backed by mechanical pumps. The cold traps were not generally used and no apparent degradation of analyzer performance has been observed in three years of operation. The typical base pressure of the system is $\approx 1 \times 10^{-7}$ torr.
The light source is pumped by a 2" NRC diffusion pump (using Convalex -10), coupled to a dry ice/acetone trap and water baffle, and is backed by a mechanical pump.

3.3. Treatment of Data

3.3.1. Energy Calibration

The photoelectron energy scales of the various molecules studied are calibrated absolutely by using UPS literature values of ionization potentials. An electron energy spectrum obtained for simultaneous Penning ionization and photoionization allows calibration of the absolute energy scale of the Penning electron spectra. To minimize any possible distortion of the Penning electron structure of the ground state ion due to overlap with photoelectron structure, the photon source is regulated such that photoelectron structure is approximately one tenth the intensity of the Penning electron structure. The accuracy of the energy scales is limited by the shape of the structure. For ideal cases, the energy scale is accurate to ± 0.010 eV.

3.3.2. Electron Analyzer Transmission Function

Since the 127° electron analyzer is operated in a constant resolution mode, the collection efficiency of the electrons varies with the electron energy due to the changing electron optical lens effects between the analyzer entrance slit and the collision chamber. If the true relative transition probabilities are to be determined and compared to those reported elsewhere, a transmission correction factor must be determined for the apparatus. The retarding analyzer of Hotop
and Niehaus\textsuperscript{45} has been reported to have a constant transmission. The integrated 90° photoionization electronic band intensities obtained in this work have been compared to the work of Hotop and Niehaus for molecular nitrogen\textsuperscript{45}, carbon monoxide\textsuperscript{45}, and nitric oxide\textsuperscript{103}, in order to derive a relative transmission correction factor, $T$, for the spectra as shown in Figure 9. In independent experiments employing electron-electron coincidence techniques, van der Wiel and Brion\textsuperscript{93} have determined the relative ionic state populations for the photoionization of carbon monoxide and found excellent agreement with the work of Hotop and Niehaus\textsuperscript{45}, as well as the total collection experiments of Frost et al.\textsuperscript{104}. As can be seen in Figure 9, there is a considerable change in the transmission function over a 12 eV range of electron energies. Failure to use the transmission correction factor $T$ would introduce serious errors in quantitative work, especially in the energy range 1 to 7 eV. The intensities of all electron spectra have been corrected, using the transmission factor $T$, in order to obtain the data reported in the tables.

3.3.3. Background Subtraction Technique.

Quantitative studies of Penning electron spectra are frequently complicated by the rapidly rising background at low electron energies. An estimation of the background electron spectrum can be obtained by removing the target gas while maintaining all other parameters necessary for operating the Penning ionization electron spectrometer. The background signal so
FIGURE 9. Relative transmission correction factor $T$ for the 127° electron analyzer.
derived may be subtracted from the observed "spectrum and background" to obtain a "background subtracted" spectrum. In a study of the Penning ionization of argon (see Figure 10, this technique was used and the subtraction was performed directly in the memory of a Fabritek 1074 multichannel analyzer. The removal of the background has extended the region where quantitative analysis may be performed by approximately 3 eV. Because of small gas dependent changes in the energy scale, this procedure is unreliable below 0.5 eV where the gradient of the background is very large.

3.4. Sample Purity.

Except for hydrogen cyanide and formaldehyde, all of the chemical samples used in this study were purchased from commercial sources and were used without further purification. The purity of all samples are listed as being better than 98%. Liquids are degassed by freeze-thaw cycles. The photoelectron spectra provide a convenient check for sample impurities. Hydrogen cyanide was prepared according to the procedure outlined by Brauer. Formaldehyde was obtained by thermal decomposition of paraformaldehyde.
FIGURE 10. Background subtraction applied to the Penning electron spectrum of argon.
4.1. Introduction.

The objective of this thesis is to continue the systematic study initiated by Stewart of the He$^+(2^1S,2^3S)$ Penning ionization of commonly available small polyatomic molecules. To date, less than sixty species have been studied by Penning ionization of which twenty-three were studied in this laboratory. The electron energy distribution of the He$^+(2^1S,2^3S)$ Penning ionization process is compared to the 584 Å photoionization process. The three general features of the electron spectra which are of interest in the comparison of the two ionization processes are the relative vibrational transition probabilities, the normalized relative electronic state populations and the $\Delta E$ energy shifts. The ratios of associative to Penning ionization have not been extracted from the electron energy distributions because the relative kinetic energy between the metastable and target species is unknown. In addition, the velocity of the metastables which leave the source have a Boltzmann's distribution.

Diatomig molecules were among the first molecules to be studied by Penning ionization with the technique of electron spectroscopy. Using a low resolution electron analyzer, Čermák studied the Penning ionization of H$_2$, N$_2$, CO, NO and O$_2$ and
observed several ionic states using both Ne*($^3P_0, ^3P_2$) and He*($^2S, ^2S$) metastable atoms. More recently, at higher resolution and using Ar*($^3P_2$) metastable atoms Čermák and Ozenne have studied the Penning ionization of NO leading to the ground state of NO$^+$ ($^1S^+\bar{X}$). Hotop and Niehaus have also studied the He*($^2S, ^2S$) and Ne*($^3P_0, ^3P_2$) Penning ionization of H$_2$, N$_2$ and CO using a high resolution electron analyzer. It is noted that in general, the observed vibrational structure of the diatomic species can be unambiguously assigned for the two modes of ionization. It also appears that for these species both $\Delta E_A$ and $\Delta E_P$ are zero, therefore, $\Delta E_{obs} = \Delta E$. In this chapter the He*($^2S, ^2S$) Penning electron spectra of H$_2$, HD, D$_2$, N$_2$, CO, NO and O$_2$ are reported.

4.2. Molecular Hydrogen, Deuterium Hydride and Molecular Deuterium.

The ground state electron configuration of these molecules are

$$(1s\sigma_g)^2 \quad ; \quad ^1\Sigma^+, (H_2, D_2)$$

$$(1s\sigma_g)^2 \quad ; \quad ^1\Sigma^+, (HD)$$

Using 584 Å photons, the photoionization of the strongly bonding $1s\sigma$ orbital consists of a single band of well resolved vibrational components, the spacing rapidly decreasing as the dissociation limit is approached. Using low resolution electron spectroscopy, Čermák studied the collision process involving He*($^2S, ^2S$) metastables with molecular hydrogen and
observed broad bands. He suggested that competing ionization processes could possibly obscure the expected vibrational structure for Penning ionization. Using mass spectrometry, Hotop and Niehaus studied the same collision process. They measured the relative ion intensities for \( \text{H}_2^+; \text{HeH}_2^+ \) and \( \text{HeH}^+ \) and concluded that although Penning ionization is the dominant process both associative ionization and dissociative associative ionization occur to a limited extent. To explain the results, they proposed a two-step model which is confirmed by independent studies by Neynaber et al. Using high resolution electron spectroscopy, Hotop and Niehaus repeated Čermák's study and they observed a single band of well resolved vibrational components.

The results for the \( \text{He}^*(2^1S,2^3S) \) Penning ionization of deuterium hydride and molecular deuterium, as well as for molecular hydrogen are now reported. Figure 11 compares the Penning electron spectra for the three molecules. The absolute energy scales are calibrated with respect to the photoelectron literature values of the ionization potentials. Table 2 shows the \( \Delta E \) shifts measured for the Penning ionization process. All peaks are shifted to higher electron energies and where comparisons are possible, the values agree with those reported by Hotop and Niehaus. The vibrational spacings for ionization by "internal" 584 Å photons as well as \( \text{He}^* (2^1S,2^3S) \) metastable atoms are indicated in Figure 11 and no differences have been observed between the two modes of ionization.
FIGURE 11. Penning electron spectra of molecular hydrogen, deuterium hydride and molecular deuterium.
Table 2.

$\Delta E_{\text{obs}}$ energy shifts in eV for the He*(2 S, 2 S) Penning ionization of molecular hydrogen, deuterium hydride, and molecular deuterium at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>$H_2^+ (^2\Sigma^+)$</th>
<th>$HD^+ (^2\Sigma^+)$</th>
<th>$D_2^+ (^2\Sigma^+)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He*(2 S)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>this work</td>
<td>$+0.088 \pm 0.020$</td>
<td>$+0.070 \pm 0.020$</td>
<td>$+0.085 \pm 0.020$</td>
</tr>
<tr>
<td>He*(3 S)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literature</td>
<td>$+0.090 \pm 0.010$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>literature</td>
<td>$+0.070$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>this work</td>
<td>$+0.069 \pm 0.010$</td>
<td>$+0.085 \pm 0.010$</td>
<td>$+0.051 \pm 0.010$</td>
</tr>
</tbody>
</table>

a. Reference 47

b. Reference 45 at ~350 °K
Extraction of the relative vibrational transition probabilities for these molecules is complicated by a number of factors. Mixed with the Penning electron spectra for He\(^*(2^1S, 2^3S)\) is a low intensity photoelectron spectrum arising from "internal" 584 Å photons\(^5\) and a rapidly rising background. The position and shape of this background appears to be dependent on the source conditions in the collision region. In addition, a large proportion of structure due to He\(^*(2^1S)\) ionization overlaps with structure due to He\(^*(2^3S)\). With the aid of a He\(^*(2^1S)\) quenching lamp, Hotop and Niehaus\(^5, 47\) have estimated the relative vibrational transition probabilities for the Penning ionization process He\(^*(2^3S)/H_2^+\) from the integral electron spectrum which is complicated by a rising background. They conclude that the Franck-Condon envelope for He\(^*(2^3S)\) Penning ionization is similar to that for photoionization by 584 Å photons.

It is not possible to evaluate the relative vibrational transition probabilities for He\(^*(2^3S)/H_2^+\) from the Penning electron spectrum in Figure 11 since this requires assumptions be made concerning the background function as well as the shape of the Franck-Condon envelope for the Penning ionization process He\(^*(2^1S)/H_2^+\). Similarly it is not possible to evaluate the relative vibrational transition probabilities for the Penning ionization of deuterium hydride or molecular deuterium. Nevertheless, an attempt was made to investigate the possible values of Franck-Condon factors for He\(^*(2^1S, 2^3S)\) Penning ionization and 584 Å photoionization\(^5\). In the upper curve of Figure 12 the
FIGURE 12. Estimation of the vibrational transition probabilities for the ionization of hydrogen.
background function of the composite curve for \( \text{H}_2^+ \) is calculated by applying to all three processes the relative vibrational intensities (corrected for transmission) as observed for external 584 Å photoionization. That is, for this operation, it is assumed that the same relative Franck-Condon factors apply irrespective of the mode of ionization. The background function so obtained is shown applied to the \( \text{N}_2^+ \) spectrum in the lower part of Figure 12 and an excellent empirical fit is obtained. This suggests that the Penning ionization of \( \text{H}_2 \) is essentially governed by the same Franck-Condon factors as photoionization.

4.3. Molecular Nitrogen.

The ground state electron configuration of the nitrogen molecule is

\[
\text{KK} \ (2s\sigma_g)^2 \ (2s\sigma_u)^2 \ (2p\pi_u)^6 \ (2p\sigma_g)^2; \ 1^1\Sigma^+ 
\]

As illustrated in Figure 13 the ionic states \( \bar{X} \ 2\Sigma^+ \), \( \bar{A} \ 2\Pi_u \) and \( \bar{B} \ 2\Pi_u^+ \) are accessible using 584 Å photons and \( \text{He}^*(2^1S, 2^3S) \) metastable atoms. The absolute energy scales are calibrated with respect to data from reference 107. The measured \( \Delta E \) energy shifts are in good agreement with the results of Hotop and Niehaus\(^5\) and are listed in Table 3. The vibrational spacings are found to be the same within experimental error for both methods of ionization, for the respective ionic states.

A quantitative analysis of the \( \text{He}^*(2^1S)/\text{N}_2^+(\bar{A} \ 2\Pi_u) \) series is not possible due to the relatively low cross-section and overlap with \( \text{He}^*(2^3S)/\text{N}_2^+(\bar{X} \ 2\Pi_g^+) \). Table 4 lists the
FIGURE 13. Electron spectra for the ionization of molecular nitrogen.
Table 3.

$\Delta E_{\text{obs}}$ energy shifts in eV for the He$^\ast(2^1S,2^3S)$ Penning ionization of molecular nitrogen at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>$X^2\Sigma^+_g$</th>
<th>$A^2\Pi_u$</th>
<th>$B^2\Sigma^+_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He$^\ast(2^1S)$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literature</td>
<td>+0.015 ± 0.010</td>
<td></td>
<td>+0.010 ± 0.010</td>
</tr>
<tr>
<td>this work</td>
<td>+0.020 ± 0.010</td>
<td>+0.023 ± 0.020</td>
<td>+0.013 ± 0.010</td>
</tr>
</tbody>
</table>

| He$^\ast(2^3S)$ |                |            |                |
| literature      | +0.050 ± 0.010 | +0.050 ± 0.010 | +0.053 ± 0.010 |
| this work       | +0.051 ± 0.010 | +0.066 ± 0.010 | +0.062 ± 0.010 |

a. Reference 45 at ~350 °K
Table 4.

Normalized relative vibrational transition probabilities for \( N_2 (\tilde{X}; v'' = 0) \rightarrow N_2^+ (\tilde{X}, \tilde{A}, \tilde{B}; v') \) for 584 Å photoionization and He*(2 S, 2 S) Penning ionization.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>( \tilde{X}^2 \epsilon_g^- )</th>
<th>( \tilde{A}^2 \pi_u^- )</th>
<th>( \tilde{B}^2 \Sigma_u^+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>He (584 Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literature(^a)</td>
<td>100</td>
<td>7(^*)</td>
<td>87(^*)</td>
</tr>
<tr>
<td>literature(^c)</td>
<td>100</td>
<td>10(^*)</td>
<td>86(^*)</td>
</tr>
<tr>
<td>this work</td>
<td>100</td>
<td>9(^*)</td>
<td>87(^*)</td>
</tr>
<tr>
<td>He*(2 S)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literature(^c)</td>
<td>100</td>
<td>12(^*)</td>
<td>89(^*)</td>
</tr>
<tr>
<td>this work</td>
<td>100</td>
<td>8(^*)</td>
<td>86(^*)</td>
</tr>
</tbody>
</table>

\(^a\) Reference 153.

\(^b\) Using 537 Å radiation.

\(^c\) Reference 45 at \( \approx 350 \, ^0\) K.
relative vibrational transition probabilities to specific ionic states. The data is in good agreement with other studies and suggests that the relative vibrational transition probabilities for the two modes of ionization are very similar for the three ionic states of nitrogen. In analyzing the results of Penning ionization of molecular nitrogen studies by optical emission spectroscopy from excited states of $N_2^+$, Robertson, Schmeltekopf et al., and Richardson and Setser have also come to the same conclusion.

Table 5 lists the relative populations of electronic states of $N_2^+$. In the case of $\text{He}^*(2^1S)$, the relative electronic population for the $N_2^+(\tilde{A}^2\Pi_u)$ state is estimated on the assumption that the Franck-Condon envelopes of $N_2^+(\tilde{X}^2\Sigma_g^+)$ are similar for Penning ionization by $\text{He}^*(2^3S)$ and photoionization using 584 Å photons. Thus, most of the structure at 3.76 eV corresponds to $\text{He}^*(2^1S)/N_2^+(\tilde{A}^2\Pi_u, v' = 1)$. It is also assumed that the ratio of the vibrational transition probability for $v' = 1$ and $v' = 2$ to the total vibration transition probability for $N_2^+(\tilde{A}^2\Pi_u)$ is similar for Penning ionization using either $\text{He}^*(2^1S)$ or $\text{He}^*(2^3S)$ metastables. The populations of electronic states obtained using $\text{He}^*(2^1S)$ metastables follow the same trend as for $\text{He}^*(2^3S)$ metastables. Comparisons of the relative population of electronic states for the two modes of ionization reveals significant population differences. For helium metastables, the relative population of the $\tilde{A}^2\Pi_u$ state is quite small, compared to that for photoionization. A comparison of the population
Table 5.
Normalized relative electronic state populations for 584 Å photoionization and He*(2 S, 2 S) Penning ionization of molecular nitrogen at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>X²Σ⁺</th>
<th>A²Π_u</th>
<th>B²Σ⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>He (584 Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literatureᵃ</td>
<td>75 ± 6</td>
<td>100 ± 6</td>
<td>17 ± 4</td>
</tr>
<tr>
<td>this work</td>
<td>79 ± 4</td>
<td>100 ± 6</td>
<td>11 ± 2</td>
</tr>
<tr>
<td>He*(1 S)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literatureᵃ</td>
<td></td>
<td>28 ± 6ᵇ</td>
<td></td>
</tr>
<tr>
<td>this work</td>
<td>100 ± 10</td>
<td>28 ± 6ᵇ</td>
<td>89 ± 18</td>
</tr>
<tr>
<td>He*(3 S)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literatureᵃ</td>
<td>85 ± 10</td>
<td>61 ± 12</td>
<td>100 ± 10</td>
</tr>
<tr>
<td>this work</td>
<td>98 ± 10</td>
<td>46 ± 5</td>
<td>100 ± 10</td>
</tr>
</tbody>
</table>

ᵃ. Reference 45 at ~350 °K
ᵇ. Estimated on the basis of v' = 1,2
ratio $\bar{X}^2\Pi_u^+ / \bar{A}^2\Pi_u^+$ reveals differences for the two modes of ionization.

In a recent study, Čermák observed electrons at 1.31 eV and 1.49 eV arising from autoionizing levels of the nitrogen atom. It has been suggested that these autoionizing levels are formed when excitation of molecular nitrogen by fast neutral He($1^1S$) atoms produces highly excited molecular states which can subsequently predissociate. There is some evidence for these two autoionizing levels in our spectrum (labeled N$^+$ in Figure 13).

4.4. Carbon Monoxide.

Carbon monoxide is isoelectronic with molecular nitrogen and has a ground state configuration of

$$\text{KK (2s}\sigma)^2 (2s\sigma^*)^2 (2p\Pi)^4 (2p\sigma)^2; 1\Sigma^+$$

For CO$^+$, the three ionic states $\bar{X}^2\Pi^+$, $\bar{A}^2\Pi$ and $\bar{B}^2\Sigma^+$ are accessible by 584 Å photons and He*(2$^1S$, 2$^3S$) metastables, (as shown in Figure 14). The process He*(2$^3S$)/CO$^+$(B $^2\Sigma^+$) is hidden in the high background at ~0.2 eV. The absolute energy scales are calibrated with respect to values given in reference 107. There is evidence of structure for He*(2$^1S$)/CO$^+$(A $^2\Pi$), but no information can be extracted since it is overlapped with the structure of "internal" He(584 Å)/CO$^+$(A $^2\Pi$).

The measured ΔE energy shifts are listed in Table 6 and are in good agreement with the work of Hotop and Niehaus $^{15}$. 
FIGURE 14. Electron spectra for the ionization of carbon monoxide.
Table 6.

$\Delta E_{\text{obs}}$ energy shifts in eV for the He$^\ast$(2$^1$S, 2$^3$S) Penning ionization of carbon monoxide at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>$\bar{X}^{2\pi^+}$</th>
<th>$\bar{A}^{2\Pi}$</th>
<th>$\bar{B}^{2\pi^+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He$^\ast$(2$^1$S)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literature$^a$</td>
<td>-0.020 ± 0.010</td>
<td>---</td>
<td>+0.040</td>
</tr>
<tr>
<td>this work</td>
<td>-0.014 ± 0.010</td>
<td>---</td>
<td>+0.049 ± 0.010</td>
</tr>
<tr>
<td>He$^\ast$(2$^3$S)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literature$^a$</td>
<td>+0.045 ± 0.010</td>
<td>+0.035 ± 0.015</td>
<td>-</td>
</tr>
<tr>
<td>this work</td>
<td>+0.043 ± 0.010</td>
<td>+0.047 ± 0.010</td>
<td>-</td>
</tr>
</tbody>
</table>

a. Reference 45 at ~350 °K
Although the orbitals available for ionization, their relative energies, and the ionic states obtained by the removal of an electron are very similar for the isoelectronic molecules nitrogen and carbon monoxide, no correlation of the ΔE energy shifts can be made. For all three ionic states of CO⁺, the vibrational spacings are the same for both modes of ionization.

The results for the relative vibrational transition probabilities for CO⁺ are listed in Table 7 and are very similar to those reported by Hotop and Niehaus⁴⁵. As in the case of nitrogen, it appears that the relative vibrational transition probabilities are very similar for given ionic states of carbon monoxide, regardless of the mode of ionization. This is the same conclusion obtained from afterglow experiments³³,³⁵,¹⁰⁸ for excited states of CO⁺.

The normalized relative population of electronic states for carbon monoxide are listed in Table 8 and agree with the values reported by Hotop and Niehaus⁴⁵. In the case of CO⁺, the ratio $X^2\Sigma^+/A^2\Pi$ is significantly different for He(584 Å) and He*(2³S). Even though the two modes of ionization are different, it is interesting to note that the ratios observed are what might be expected on the basis of the relative populations of states of CO⁺ which have been measured as a function of "photon" energy by van der Wiel and Brion⁹³. Comparisons of the relative population of electronic states for a given mode of ionization are found to be very similar for
Table 7.
Normalized relative vibrational transition probabilities for CO (X, v" = 0) + CO⁺(X,A,B; v') for 584 Å photoionization and He*(2¹S,2³S) Penning ionization.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>Χ²⁺</th>
<th>Α²π</th>
<th>Β²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0,1</td>
<td>0,1</td>
<td>0,1</td>
</tr>
<tr>
<td>He (584 Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>this work</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>this work</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>He*(2¹S)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>this work</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>He*(2³S)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>this work</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

b. 537 Å.
c. Reference 45 at ~350 K.
d. Some contributions due to He*(2¹S) and He (584 Å).
Table 8.

Normalized relative electronic state populations for 584 Å photoionization and He*(2^1S,2^3S) Penning ionization of carbon monoxide at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>2^+ X Σ</th>
<th>2^- A Π</th>
<th>2^+ B Σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>He (584 Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literaturea</td>
<td>67 ± 7</td>
<td>100 ± 6</td>
<td>19 ± 4</td>
</tr>
<tr>
<td>this work</td>
<td>70 ± 4</td>
<td>100 ± 10</td>
<td>9 ± 2</td>
</tr>
<tr>
<td>He*(2^1S)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literaturea</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>this work</td>
<td>96 ± 10</td>
<td>?</td>
<td>100 ± 25</td>
</tr>
<tr>
<td>He*(2^3S)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literaturea</td>
<td>100</td>
<td>43 ± 10</td>
<td>—</td>
</tr>
<tr>
<td>this work</td>
<td>100 ± 10</td>
<td>38 ± 6</td>
<td>—</td>
</tr>
</tbody>
</table>

a. Reference 45 at ~350 °K
both carbon monoxide and nitrogen. No data could be obtained for the process \( \text{He}^*(2^3S)/\text{CO}^+(\bar{E}^2\Sigma^+) \) which is probably hidden in the rapidly rising background. However, the ratio \( \bar{X}^2\Sigma^+/A^2\Pi \) for the population of ionic states formed using \( \text{He}^*(2^3S) \) is found to be very similar for both molecular nitrogen and carbon monoxide.

There is some evidence to suggest that carbon monoxide may be excited into a highly excited predissociating state by fast neutral helium atoms. After dissociating, the products may be in an autoionizing state. For example, in the Penning electron spectra of carbon monoxide, there are two unidentified peaks in Figure 14 labeled \( 0^+ \) at 1.77 eV and 1.55 eV. These values correspond closely to electron ejection energies from autoionizing states of the oxygen atom as observed by Čermák and Šrámek\(^{110}\). It is noted that the peak at 1.55 eV could also correspond to structure due to \( \bar{E}^2\Sigma^+, \nu' = 0 \), for the 584 Å photoionization of \( \text{N}_2 \).

4.5. Nitric Oxide.

The ground state electron configuration for nitric oxide is

\[
\text{KK} \ (2s\sigma)^2 \ (2s\sigma^*)^2 \ (2p\pi)^2 \ (2p\pi^*)^4 \ (2p\pi^*)^1 \ ; \ 2\Pi
\]

In the \( \text{He}(584 \text{ Å}) \) photoionization spectrum of nitric oxide, eight of the ionic states have been identified\(^{111}\). A number of laboratories\(^{37,46,49}\) have studied aspects of the Penning ionization electron spectroscopy of nitric oxide, in particular comparing the Penning ionization and photoionization relative
vibrational transition probabilities for $\text{NO}^+(\tilde{X}^1\Sigma^+)$. It has been concluded that if there is a difference in the Franck-Condon factors for the two modes of ionization, it is small.

Figure 15 compares the Penning electron spectrum and the photoelectron spectrum of nitric oxide. In the He*(2^1S) Penning electron spectrum, structure for $\tilde{X}^1\Sigma^+$ and $\tilde{a}^3\Pi$ states of NO$^+$ is observed. For He*(2^3S) ionization, structure is observed for the $\tilde{X}^1\Sigma^+$, $\tilde{a}^3\Pi$ and $\tilde{A}^1\Pi$ states. The $\Delta E$ energy shifts for nitric oxide are listed in Table 9. Both the vibrational spacings and the associated Franck-Condon factors for the NO$^+(\tilde{X}^1\Sigma^+)$ state for the two modes of ionization are found to be the same, within experimental error, as reported earlier. It appears that the relative populations of the three electronic states $\tilde{X}^1\Sigma^+$, $\tilde{a}^3\Pi$ and $\tilde{A}^1\Pi$ as shown in Table 10 are also very similar for ionization by He*(2^3S) metastables and 584 Å photons.

There appears to be evidence for autoionization of dissociation products of nitric oxide excited by fast neutral helium atoms in that there is structure in the region of 1.7 eV to 3.0 eV which cannot be accounted for by Penning ionization. The energy of some of these peaks agree with electron ejection energies from autoionizing levels of the oxygen atom as observed by Čermák. In addition, there are two peaks at 0.6 eV and 1.1 eV labeled $N^+$, which correspond to two autoionizing levels in the nitrogen atom also observed by Čermák.
FIGURE 15. Electron spectra for the ionization of nitric oxide.
Table 9.

$\Delta E_{\text{obs}}$ energy shifts in eV for the He$^*$(2$^1$S, 2$^3$S) Penning ionization of nitric oxide at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>$\tilde{X}^1\Sigma^+$</th>
<th>$\tilde{b}^3\Pi$</th>
<th>$\tilde{A}^1\Pi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He$^*$(2$^1$S)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literature$^a$</td>
<td>+0.00 ± 0.010</td>
<td>+0.00 ± 0.010</td>
<td></td>
</tr>
<tr>
<td>this work</td>
<td>+0.007 ± 0.020</td>
<td>+0.018 ± 0.020</td>
<td></td>
</tr>
<tr>
<td>He$^*$(2$^3$S)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literature$^a$</td>
<td>-0.010 ± 0.010</td>
<td>+0.035 ± 0.010</td>
<td></td>
</tr>
<tr>
<td>this work</td>
<td>-0.009 ± 0.015</td>
<td>+0.062 ± 0.015</td>
<td>+0.032 ± 0.015</td>
</tr>
</tbody>
</table>

$^a$ Reference 103
Table 10.
Normalized relative electronic state populations for 584 Å
photoionization and He*(2 S) Penning ionization of nitric oxide
at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>$^1\Sigma^+$</th>
<th>$^3\Pi^+$</th>
<th>$^1\Pi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He (584 Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literature $^a$</td>
<td>32</td>
<td>100</td>
<td>40</td>
</tr>
<tr>
<td>literature $^b$</td>
<td>40 ± 3</td>
<td>100</td>
<td>52 ± 8</td>
</tr>
<tr>
<td>this work</td>
<td>33 ± 2</td>
<td>100 ± 5</td>
<td>45 ± 9</td>
</tr>
<tr>
<td>He*(2 S)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literature $^b$</td>
<td>29 ± 5</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>this work</td>
<td>35 ± 4</td>
<td>100 ± 9</td>
<td>50 ± 9</td>
</tr>
</tbody>
</table>

$^a$ Reference 111

$^b$ Reference 103

Molecular oxygen has a ground state configuration of
\[ \text{KK} (2s\sigma_g)^2 (2s\sigma_u)^2 (2p\sigma_g)^2 (2p\pi_u)^4 (2p\pi_g)^2; \quad ^3\Sigma^- \]

Edqvist et al.\textsuperscript{112} have studied both the 584 Å and the 304 Å photoelectron spectra of molecular oxygen. Using 584 Å photons, it is possible to observe five ionic states (see Figure 16) of molecular oxygen. However, in the Penning electron spectrum only the \( \text{O}_2^+ (\overline{\Xi} \, 2\Pi_g) \) state produced by He\*(2\(^3\)S) metastables can be clearly identified. There is some evidence for the \( \overline{\Xi} \) state of \( \text{O}_2^+ \) produced by He\*(2\(^1\)S) metastables but quantitative measurements are not possible. The vibrational spacings for the ground ionic state (\( \overline{\Xi} \, 2\Pi_g \)), as indicated in Figure 17, are the same within experimental error for both modes of ionization.

The \( \Delta E \) energy shift measured for He\*(2\(^3\)S)/\( \text{O}_2^+ (\overline{\Xi} \, 2\Pi_g) \) is \(-0.019 \pm 0.010 \) eV. For He(584 Å)/\( \text{O}_2^+ (\overline{\Xi} \, 2\Pi_g) \) and He\*(2\(^3\)S)/\( \text{O}_2^+ (\overline{\Xi} \, 2\Pi_g) \) the relative vibrational populations are listed in Table 11.

Comparison of the data in Table 11 for the two processes indicates significant differences for Penning ionization and photo-ionization at higher vibrational quantum numbers. Distortion of the Franck-Condon factors in the Penning ionization of molecular oxygen has also been observed by Richardson et al.\textsuperscript{34,35} for the \( \text{O}_2^+ (\overline{\Xi} \, 2\Pi_u) \) ionic state. This distortion of the Franck-Condon envelopes in Penning ionization possibly suggests that the potential curves for \( \text{O}_2 \) and/or \( \text{O}_2^+ \) are perturbed by the helium particles. In a recent study of the angular distributions of Penning ions, Leu and Siska\textsuperscript{32} have proposed a modification of
FIGURE 16. Electron spectra for the ionization of molecular oxygen.
FIGURE 17. Electron spectra for the ionization of $O_2$ to $O_2^+(\bar{X}^2\pi_g)$. 
Table 11.

Normalized relative vibrational transition probabilities for \( O_2 (\bar{X},v'' = 0) + O_2^+ (\bar{X}^1\Pi_g, v') \) for 584 Å photoionization and He*(2S) Penning ionization.

<table>
<thead>
<tr>
<th>( v' )</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>He (584 Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>literature\textsuperscript{a}</td>
<td>43</td>
<td>100</td>
<td>92</td>
<td>45</td>
<td>14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>literature\textsuperscript{b}</td>
<td>45</td>
<td>100</td>
<td>92</td>
<td>50</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>this work</td>
<td>46 ( \pm ) 3</td>
<td>100</td>
<td>95 ( \pm ) 4</td>
<td>49 ( \pm ) 3</td>
<td>15 ( \pm ) 2</td>
<td>2 ( \pm ) 1</td>
<td></td>
</tr>
<tr>
<td>He* (2S)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>this work</td>
<td>47 ( \pm ) 5</td>
<td>100</td>
<td>93 ( \pm ) 5</td>
<td>61 ( \pm ) 5</td>
<td>37 ( \pm ) 5</td>
<td>17 ( \pm ) 5</td>
<td>9 ( \pm ) 5</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reference 103

\textsuperscript{b} Reference 112
the potential curve model for Penning ionization. They have concluded that relative to the He\(^*(2^1S)\) Penning ionization of \(H_2\), \(N_2\) and \(CO\), the collision with \(O_2\) is much harder and reactive due to a lowering or absence of an entrance barrier. Due to these harder and more reactive collisions, perturbation of the two potential curves would not be unexpected.

Distortion of the Franck-Condon factors may also be explained by the possibility of a competing autoionization leading to \(O_2^+(\Phi \, ^2\Pi_g)\). Natalis and Collin\(^85\) suggest that autoionization will explain the anomalous Franck-Condon factors for \(O_2^+(\Phi \, ^2\Pi_g)\) produced by photoionization of \(O_2\) using \(Ne(736,744 \, \AA)\) radiation. The possibility of similar competing modes of ionization in metastable atom collisions have been discussed by Herman and Čermák\(^113\). It is now suggested that autoionization may also compete with the Penning ionization of molecular oxygen when \(He^*(2^3S)\) metastables are used. It is possible that the oxygen molecule may be excited to an autoionizing level by resonant excitation transfer with \(He^*(2^3S)\) metastable atoms. Some evidence for this is provided by the fact that Geiger and Schröder\(^114\) have observed a member of a Rydberg series at 19.810 eV, converging to the ionization limit of \(O_2^+ (\Phi \, ^2\Sigma^-_g, v' = 2)\) (the energy of \(He^*(2^3S)\) is 19.818 eV). Photoabsorption studies by Huffman et al.\(^115\) also indicate the existence of this excited state of \(O_2\). Since the difference in energies between the Rydberg states of \(O_2\) and \(He^*(2^3S)\) is small, the cross-section for excitation transfer may be large enough to populate the Rydberg
state to a significant degree. No Rydberg states were observed in the region of 20.615 eV (the energy of He^+(2^1S)). West et al. have indicated that an excited oxygen molecule, O_2**, is formed in a significant fraction of the He^+(2^1S,2^3S) collisions with O_2.

With the exception of the O_2^+(X^2Π_g) state, the Penning electron spectrum cannot be assigned since it is apparently overlapped with structure due to other unidentified processes. The degree to which associative ionization competes with Penning ionization is not known. In a study of the chemi-ionization of oxygen molecules by He^+(2^1S,2^3S) metastables, West et al. have proposed the formation of a temporary (HeO_2)^* molecule which then may either autoionize to the HeO_2^+ continuum or fragment. Data appear to be consistent with this proposed mechanism and suggest that the probability of forming the temporary (HeO_2)^* molecule is relatively large. Structure in the energy range 0-4 eV of the electron spectra (Figure 18) resembles that which Čermák and Šrámek have assigned to processes resulting from collisions between O_2 and fast neutral helium atoms. The role of fast neutral helium atom interactions with rare gas atoms has been discussed. The large magnitude of the structure found for O_2 may suggest that the ratio of the cross-sections, for processes involving fast (600 eV) neutral helium atoms to those for Penning ionization by thermal metastable helium atoms is large relative to the situation for N_2, CO and NO. It is also possible that some of this structure is due to autoionization of excited oxygen atoms formed by dissociation of
FIGURE 18. Electron spectra for the ionization of molecular oxygen.
excited O₂** formed by excitation transfer from helium metastable atoms (below ~1.9 eV). The peaks observed by Čermák and Šrámek¹¹⁰ are shown by the vertical marks on Figure 18. Most of these peaks have also been observed by Rudd and Smith¹¹⁷ in the ejected electron spectra resulting from O₂ excitation by 100 keV H⁺ and He⁺. Using ionization energies and vibrational spacings from the 584 Å photoionization studies of O₂ by Edquist et al.¹¹² it is possible to calculate the expected positions (shown on Figure 18) of the bands for various Penning ionization processes assuming the energy shifts, ΔE, to be zero. It is possible that the broad band between 3.7 and 2.5 eV is due at least in part to the process He*(2⁺S)/O₂⁺(a ¹Πₜ) (Čermák and Šrámek¹¹⁰ have attributed the peak at 1.67 eV to production of O(3d', ³P) followed by autoionization to O⁺.) However this peak may be due to He*(2⁺S)/O₂⁺(5 ⁴Σ₋ₕ, ν' = 0) which would be at 1.65 eV (assuming ΔE = 0). The spectrum also shows (figure 18) a shoulder corresponding to ν' = 1 as well as peak close to the energy expected for ν' = 2. It should be noted that our assignments of the spectrum in this region differ somewhat from those given by Čermák to Šrámek. The calculated position for the ν' = 0 level of He*(2¹S)/O₂⁺(5 ⁴Σ₋ₕ) lies between peaks at 2.48 and 2.36 eV reported by Čermák and Šrámek and there is some indication (Figure 18) of a small peak on top of the underlying structure. Apart from these differences generally good agreement is obtained with the structure and assignments reported by Čermák and Šrámek. Some differences might be expected for those processes due to fast neutral helium atoms since in this experiment the energy of the fast neutral is 600 eV compared to 250 eV in the work of Čermák and Šrámek.
CHAPTER FIVE

SIMPLE POLYATOMIC MOLECULES

5.1. Introduction.

Ammonia was one of the first molecules to be studied by Penning ionization using the technique of electron spectroscopy\(^2\). Using a low resolution electron spectrometer, Čermák studied the Ne\(^*(3P_0,3P_2)\) Penning ionization of ammonia. From this data, an unusually large \(\Delta E_{\text{obs}}\) energy shift of \(-0.24\) eV can be derived for the \(\tilde{X}^2A_2^+\) ionic state of ammonia. The ratio of the populations of the ionic states could not be determined. Čermák\(^2\) also has studied ethylene with both Ne\(^*(3P_0,3P_2)\) and He\(^*(2^1S,2^3S)\) metastable atoms and observed several ionic states. More recently, at higher resolution and using Ar\(^*(3P_0,3P_2)\) metastable atoms, Čermák and Ozenne\(^3\) have studied the Penning ionization of ethylene leading to the ground state of \(C_2H_4^+\). In this chapter are reported the quantitative comparisons of the He\(^*(2^1S,2^3S)\) Penning ionization and the 584 Å photoionization of \(NH_3, PH_3\) and \(C_2H_4\).

5.2. Ammonia.

Ammonia belongs to the point group \(C_{3v}\) and the ground state electron configuration can be written as

\[(1a_1)^2 (2a_1)^2 (1e)^4 (3a_1)^2 \ ; \ ^1A_1\]
The equilibrium geometry of the ammonia ion in its ground state is near planar\textsuperscript{118,119} and it can therefore be considered as belonging to the point group D\textsubscript{3h}. The ground state electron configuration of the ammonia ion can be written as

$$(1a_1')^2 (2a_1')^2 (1e')^4 (1a_2''); ^2A_2''$$

In Figure 19, the Penning electron spectrum of NH\textsubscript{3} is compared to the 584 Å photoelectron spectrum. The photoelectron spectrum of NH\textsubscript{3} is well known and has been discussed in detail\textsuperscript{118-121}. The first band, $\tilde{X}^2A_2''$, of the photoelectron spectrum consists of a well resolved vibrational progression involving a single fundamental frequency $v_2$, the totally symmetric out of plane bending mode\textsuperscript{120}. The vertical ionization potential\textsuperscript{120} for the $\tilde{X}^2A_2''$ ionic state at 10.87 eV ($v' = 6$) in the photoelectron spectrum is used to calibrate the absolute energy scale of the Penning electron spectrum. The second band $\tilde{A}^2E'$ of the photoelectron spectrum consists of a broad band with no well resolved structure.

The Penning electron spectrum of NH\textsubscript{3} is shown in the upper part of Figure 19. The lack of vibrational structure in the first band is probably due to the intrinsic width of Penning ionization structure\textsuperscript{51}, therefore it is not possible to evaluate the true $\Delta E$ from $\Delta E_{\text{obs}}$. Although the presence of the $\tilde{A}^2E'$ state is apparent from the Penning spectrum, quantitative measurements are precluded because of the rapidly rising background at lower electron energies. After the background subtraction technique is performed, quantitative analysis of both states is
FIGURE 19. Electron spectra for the ionization of ammonia.
The Penning spectrum of NH$_3$ (Figure 19) evidently contains contributions from both He$^*(2^1S)$ and He$^*(2^3S)$ although the separate structures cannot be resolved because of the broad bands. It is reasonable to assume that most (~90%) of the structure is from He$^*(2^3S)$, in view of the relatively low contribution for He$^*(2^1S)$ observed with this spectrometer for atoms$^{50}$ and molecules$^{51}$. These conclusions are also supported by examining the narrower bands in the PH$_3$ spectrum (Figure 20) where the He$^*(2^1S)$ contributions can be estimated. On this basis the relative band areas for Penning ionization and photoionization are compared. The normalized relative electronic state populations for each ionizing mode can be seen to be quite different (Table 12). In a coincidence experiment van der Wiel and Brion$^{99}$ measured the partial photoionization cross-sections (including the $\beta$ dependence) for the three lowest ionic states of ammonia as a function of photon energy. For the $\bar{X}^2A^+_2$ state, the cross-section decreases with energy while for the $\bar{A}^2E'$ state, the cross-section increases with energy in the range 19.8 eV to 21.2 eV. Although these results are for photoionization, this type of behaviour may in part explain the observed differences in the relative state populations.

The $\Delta E_{obs}$ energy shift for the process He$^*(2^3S)/$NH$_3^+$ ($\bar{X}^2A^+_2$) has the unusually large value of $-0.41 \pm 0.05$ eV (see Figure 19). It should be noted that this is an order of magni-
Table 12.

$\Delta E_{\text{obs}}$ energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*(2\(^3\)S) Penning ionization of ammonia at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>$\Delta E_{\text{obs}}$ (eV)</th>
<th>584 Å (21.22 eV)</th>
<th>He*(2(^3)S) (19.82 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X^2 \text{A}_2^+$</td>
<td>-0.41 ± 0.05</td>
<td>100 ± 20</td>
<td>100 ± 10\text{a}</td>
</tr>
<tr>
<td>$\text{A}^2 \text{E}'$</td>
<td>—</td>
<td>400 ± 40</td>
<td>64 ± 6 \text{a}</td>
</tr>
</tbody>
</table>

\text{a.} Obtained from "Background Subtracted Spectrum" and includes minor contribution from He*(2\(^1\)S) and He (584 Å).
tude large than $\Delta E_{\text{obs}}$ values observed for previously studied atoms$^{50}$ and molecules$^{51}$, but is comparable in magnitude to the 
-0.24 eV shift observed by Čermák$^{28}$ for the process $\text{Ne}^+(3^3\text{P}_0, 3^3\text{P}_2)$ 
$/\text{NH}_3^+(\bar{X}^2\text{A}_2^\text{e})$. A possible suggestion is that a shift of the 
observed maximum of the Franck-Condon envelope to higher vibra-
tional quantum numbers might produce the large $\Delta E_{\text{obs}}$ energy 
shift observed. This may occur as a result of the shape of the 
ingoing and outgoing potential surfaces and the transition 
probability for Penning ionization. It is possible that an 
alternative autoionization process via excitation transfer$^{51}$ 
might shift the observed maximum of the Franck-Condon envelope. 
No value for the $\Delta E_{\text{obs}}$ shift of the $\bar{A}^2\text{E}'$ state is given because 
of the relatively large uncertainty involved in locating the 
position of the peak maximum.

5.3. Phosphine.

Phosphine is the second row analogue of ammonia and 
also belongs to the point group $C_{3v}$. The ground state electron 
configuration of phosphine is 

$\text{[1a}_1^2 \text{2a}_1^2 \text{1e}^4 \text{3a}_1^2 \text{4a}_1^2 \text{2e}^6 (5\text{a}_1)^2; \text{1A}_1}$ 

Unlike ammonia, the ground state of the ion of phosphine is 
pyramidal$^{119,120}$ so it also belongs to the point group $C_{3v}$.

Figure 20 compares the Penning electron and photoelectron 
spectrum of phosphine. The photoelectron spectrum of phosphine 
is very similar to that of ammonia. The first vibrational 
progression, $\bar{X}^2\text{A}_1$, of phosphine is assigned to $v_2$, the totally 
symmetric out of plane bending mode$^{122}$. The vertical ionization
FIGURE 20. Electron spectra for the ionization of phosphine.
potential$^{122}$ is 10.59 eV which corresponds to $v' = 9$. The second band of phosphine, $\tilde{X} \; ^2E$, is broad with no well resolved structure. The Penning electron spectrum of phosphine (Figure 20) is also qualitatively very similar to that for ammonia. Since vibrational structure is not observed, it is not possible to evaluate the true $\Delta E$ from $\Delta E_{\text{obs}}$. A small shoulder on the $\tilde{X} \; ^2A_1$ band is from ionization by He*(2$^1$S) metastable atoms. However, it appears that most (~90%) of the structure in the first peak is a result of electrons ejected in collisions of PH$_3$ with He*(2$^3$S) metastable atoms. Background subtraction is used to obtain the quantitative data shown in Table 13. Within experimental error, values from the background subtracted data agree with values derived from the "spectrum plus background" data. This lends some confidence to the background subtraction procedure. As in the case of ammonia, the normalized relative populations of electronic states of PH$_3$ show significant differences for photoionization and Penning ionization (see Table 13). For Penning ionization, the relative populations are estimated for the sum of He*(2$^1$S) and He*(2$^3$S) metastable states, but as discussed earlier, the He*(2$^3$S) contributions will be dominant.

The $\Delta E_{\text{obs}}$ energy shift of the $\tilde{X} \; ^2A_1$ state formed by He*(2$^3$S) metastable is $+0.10 \pm 0.05$ eV. The absolute value of this $\Delta E_{\text{obs}}$ energy shift is fairly large relative to values observed for other molecules$^{50,51}$ but it is somewhat smaller in magnitude than the value of $-0.41$ eV found for ammonia. No value for the $\Delta E_{\text{obs}}$ energy shift of the $\tilde{A} \; ^2E$ state is given due
Table 13. 

$\Delta E_{\text{obs}}$ energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization He$^*(2^3 S)$ Penning ionization of phosphine at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>$\Delta E_{\text{obs}}$ (eV)</th>
<th>Relative State Populations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X^2 A_1$</td>
<td>+0.10 ± 0.05</td>
<td>100 ± 22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100 ± 10$^a$</td>
</tr>
<tr>
<td>$A^2 E$</td>
<td>—</td>
<td>455 ± 45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>67 ± 7 $^a$</td>
</tr>
</tbody>
</table>

$^a$ Obtained from "Background Subtracted Spectrum" and includes minor contribution from He$^*(2^1 S)$ and He (584 Å).
to the relatively large uncertainty involved in locating the position of the peak maximum.

It is interesting to note in comparing ammonia and phosphine that the relative population of ionic states is very similar for the two molecules for a given ionization mode.

5.4. Ethylene.

Ethylene is isoelectronic with oxygen and it is the simplest organic molecule to contain a carbon-carbon bond. The electron configuration of ethylene is described by

\[ \ldots (2a_g)^2 (1b_1u)^2 (1b_2u)^2 (3a_g)^2 (1b_3g)^2 (1b_3u)^2 ; 1a_g \]

In the lower section of Figure 21, the 584 Å photoelectron spectrum of ethylene is shown. The spectrum is similar to that observed by Branton et al.\textsuperscript{120} and by Baker et al.\textsuperscript{123} who have analyzed the complex fine structure of the photoelectron bands.

The top section of Figure 21 shows the He*(2\textsuperscript{1}S,2\textsuperscript{3}S) Penning electron spectra of C\textsubscript{2}H\textsubscript{4}. Utilization of the background subtraction technique\textsuperscript{52} on the ethylene data is less effective than with some other molecules but nevertheless it allows for more accurate quantitative measurements to be made in the region of the steeply rising background. The four ionic states observed in the photoelectron spectrum are also observed in the He*(2\textsuperscript{3}S) Penning electron spectra and there is evidence for some vibrational structure. This vibrational structure can be unambiguously assigned and it appears that both \( \Delta E_A \) and \( \Delta E_p \) are zero, therefore,
FIGURE 21. Electron spectra for the ionization of ethylene.
\( \Delta E_{\text{obs}} = \Delta E \). Using \( \text{He}^*(2^1S) \) metastable atoms, structure is only evident for the process \( \text{He}^*(2^1S)/\text{C}_2\text{H}_4^+ (X^2B_{3u}) \). The \( \text{He}^*(2^1S) \) contribution is approximately 20% and to this extent there will probably be overlapping \( \text{He}^*(2^1S) \) contributions to the spectrum. The \( \Delta E \) energy shift values, which are parameters reflecting the nature of interactions in the collision process\(^5\), are listed in Table 14. These values are determined with respect to the measured photoionization ionization potentials and are the average values over the vibrational bands. These measured values are typical of measurements made on other molecules\(^5\).

A detailed comparison of the 584 Å photoelectron spectrum and the \( \text{He}^*(2^1S,2^3S) \) Penning electron spectrum of the first band of \( \text{C}_2\text{H}_4^+ (X^2B_{3u}) \) is shown in Figure 22. The markers in the photoionization spectrum indicate the vibrational levels for the vibrational modes \( v_2 \) and \( v_4 \).\(^{120,123} \) The structure in the \( \text{He}^*(2^3S) \) Penning electron spectrum is broadened due to the Penning process and this makes the assignment of the first vibration more difficult. Markers indicate the assignment of the vibrational levels for the vibrational modes \( v_2 \) and \( v_4 \) for \( \text{He}^*(2^3S) \) Penning ionization. No vibrational structure is resolved for the process \( \text{He}^*(2^1S)/\text{C}_2\text{H}_4^+ (X^2B_{3u}) \) (in other molecules\(^5\), the bands due to \( \text{He}^*(2^1S) \) are also very broad). The Franck-Condon envelope for the \( \text{C}_2\text{H}_4^+ (X^2B_{3u}) \) state is, within experimental error, the same for both \( \text{He}^*(2^3S) \) Penning ionization and 584 Å photoionization. For the \( \text{He}^*(2^3S)/\text{C}_2\text{H}_4^+ (A^2B_{3g}) \) process (Figure 21) the Franck-Condon envelope is also found to be very similar.
Table 1.

$\Delta E_{\text{obs}}$ energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*$(2^3S)$ Penning ionization of ethylene at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>$\Delta E_{\text{obs}}$ (eV)</th>
<th>$584 ,^0\text{Å}$ (21.22 eV)</th>
<th>He*$(2^3S)$ (19.82 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X^2 \text{B}_3\text{u}$</td>
<td>-0.020 ± 0.020</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>$A^2 \text{B}_3\text{g}$</td>
<td>+0.038 ± 0.020</td>
<td>177 ± 20</td>
<td>21 ± 1&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>$B^2 \text{A}_2\text{g}$</td>
<td>-0.041 ± 0.030</td>
<td>229 ± 30</td>
<td>23 ± 2&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>$C^2 \text{B}_2\text{u}$</td>
<td>+0.037 ± 0.030</td>
<td>150 ± 20</td>
<td>27 ± 3&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Contains small contributions from He*$(2^1S)$ and He (584 Å).
C₂H₄

Photolionization (584 Å)

ELECTRON ENERGY (eV)

FIGURE 22. Electron spectra for the ionization of ethylene to the ground state ion (X²B₃ᵤ)
to that for the 584 Å photoionization process. Sufficiently accurate measurements of the Franck-Condon envelope cannot be made for either of the processes He*(2^3S)/C\textsubscript{2}H\textsubscript{4}+(B\textsuperscript{2}A\textsubscript{g}) and He*(2^3S)/C\textsubscript{2}H\textsubscript{4}+(C\textsuperscript{2}B\textsubscript{2}u).

In Table 14 the normalized relative populations of the electronic states of C\textsubscript{2}H\textsubscript{4}+ are compared for the two modes of ionization. The data are arbitrarily normalized with respect to the C\textsubscript{2}H\textsubscript{4}+(X\textsuperscript{2}B\textsubscript{3}u) state. It is noted that very large relative differences occur. This suggests that there may be large differences in relative partial cross-sections for the two modes of ionization. It is unlikely that the large differences in the relative populations are due only to the differences in the angular distributions for electrons ejected from the different ionic states\textsuperscript{51}. It is noted that ideally the He*(2^1S) Penning electron spectrum should be compared to the 601 Å photoelectron spectrum and the He*(2^3S) Penning electron spectrum should be compared to the 626 Å photoelectron spectrum. Measurements of partial cross-sections as a function of excitation energy for the photoionization of molecules\textsuperscript{93-95} indicate that the relative state populations can change significantly even over a few electron volts.
CHAPTER SIX

HYDROGEN CYANIDE AND SOME RELATED COMPOUNDS

6.1. Introduction.

Recent studies in this laboratory of the photoelectron spectroscopy\textsuperscript{124} and electron impact excitation\textsuperscript{125} of HCN has prompted this investigation of the He*\((2^1S,2^3S)\) Penning ionization of this molecule and some related compounds. Fridh and \textsuperscript{\textregistered} Asbrink\textsuperscript{126} have recently reported high resolution 584 Å photoelectron spectroscopy data for HCN. Urisu and Kuchitsu\textsuperscript{127} and Coxon et al.\textsuperscript{128} have analyzed the emission from excited states of CN produced by the dissociation of HCN, BrCN and ICN in Ar*\((3P_0,3P_2)\) and Xe*\((3P_2)\) afterglows. This suggests that when using He*\((2^1S,2^3S)\) metastables that in addition to Penning ionization, there is a possibility that autoionizing states of CN may be observed. Dibeler and Liston\textsuperscript{129} have studied the photoionization-yield curves for dicyanogen and the cyanogen halides from threshold to 600 Å.

In this chapter the He*\((2^1S,2^3S)\) Penning ionization of HCN, \((CN)_2\), CH\textsubscript{3}CN, BrCN and ICN are reported. The He*\((2^1S,2^3S)\) Penning ionization process is compared to that of 584 Å photo-ionization. A search is also made for evidence of other chemi-ionization processes.

HCN has the ground state molecular orbital configuration\(^1\text{30}\)

\((1\sigma)^2 (2\sigma)^2 (3\sigma)^2 (4\sigma)^2 (5\sigma)^2 (1\pi)^4\); \(^1\Sigma^+\)

where the \(1\pi\) orbital is the \(\pi\)-bonding orbital and the \(5\sigma\) orbital is the nitrogen lone pair orbital.

In Figure 23 the He\(^*(2^1S,2^3S)\) Penning electron and the 584 Å photoelectron spectra of HCN are compared. The photoelectron spectrum, indicating three ionic states, is very similar to that reported by Baker and Turner\(^1\text{31}\). The complex first band in the 584 Å photoelectron spectrum has been analyzed in detail at higher resolution by Frost et al.\(^1\text{24}\) and Fridh and Asbrink\(^1\text{26}\).

The He\(^*(2^1S,2^3S)\) Penning electron spectrum shows structure only for the He\(^*(2^3S)/HCN^+\(X^2\Pi\)) and the He\(^*(2^3S)/HCN^+\(A^2\Sigma\)) processes. The higher band observed in the photoelectron spectrum is too close to the zero energy cut off to be seen in the Penning electron spectra. The relatively large \(\Delta E_{\text{obs}}\) energy shifts for these two bands are \(-0.15 \pm 0.10\) and \(-0.14 \pm 0.05\) eV respectively. Although there is some indication of vibrational structure for these two bands a unique assignment of the vibrational levels is not possible (Figure 23b). Consequently, \(\Delta E\) values cannot be calculated from \(\Delta E_{\text{obs}}\)\(^5\text{4}\). The tentative vibrational assignment (which assumes \(\Delta E_A = 0\)) shown above the Penning electron bands in Figure 23b would result in a \(\Delta E\) value very close to zero for both states. This assignment would mean that the positions of the maxima of the Franck-Condon envelopes for Penning ionization and photoionization correspond to different vibrational levels.
FIGURE 23. Electron spectra for the ionization of hydrogen cyanide. a. full spectra b. first band including 584 Å calibration.
This type of phenomenon appears to occur for Penning ionization to the ground state of the ions of water and related molecules\(^5\) and suggests that some appreciable modification of the target potential surfaces may be occurring. An alternative assignment (i.e., shifting by one or more vibrational quanta) would mean that \(\Delta E\) would have correspondingly large negative values, whereas for most of the other atoms and molecules\(^50-52\) studied, \(\Delta E < |0.1|\) eV (i.e., of the order of thermal energies).

A quantitative analysis of the relative populations of electronic states of HCN\(^+\) for both Penning ionization and photoionization is not possible because the two ionic states are not completely separated. Quantitative information for the 584 Å photoionization process could be obtained from the higher resolution spectrum (deconvoluted) reported by Fridh and Åsbrink\(^12\) if the electron transmission efficiency of their analyzer was known. A qualitative analysis of the relative populations of electronic states of HCN (Figure 23) reveals large differences when comparing the two modes of ionization. In particular it appears that the partial ionization cross-section for production of the \(\tilde{X}\) 2\(\Pi\) state of HCN\(^+\) relative to that for the \(\tilde{A}\) 2\(\Sigma\) state is much smaller for Penning ionization than for photoionization.

6.3. Dicyanogen.

The ground state electron configuration of (CN)\(_2\) is\(^13\)  
\[ ... (3\sigma_g)^2 (3\sigma_u)^2 (4\sigma_g)^2 (1\Pi_u)^4 (4\sigma_u)^2 (5\sigma_g)^2 (1\Pi_g)^4; 1\Sigma^+ \]

The wavefunctions for the 1\(\Pi_g\) and the 1\(\Pi_u\) orbitals can be represented by the out of phase and the in phase combination of
the Π bonding orbitals while the 4σ_u and the 5σ_g orbitals can be represented by the out of phase and the in phase combinations of the nitrogen non-bonding orbitals\textsuperscript{131}.

In Figure 24 the He\#(2\textsuperscript{1}S,2\textsuperscript{3}S) Penning electron and the 584 Å photoelectron spectra of (CN)\textsubscript{2} are compared. The photoelectron spectrum is very similar to that reported in other studies\textsuperscript{130-132}. The same four ionic states observed in the photoelectron spectrum are also observed in the Penning electron spectrum. The ΔE\textsubscript{obs} energy shift values are listed in Table 15. For the ground state of the ion, ΔE\textsubscript{obs} = ΔE, since the peak maximum of the resolved vibrational structure corresponds to the same vibrational level (ν' = 0). ΔE is small in magnitude (i.e., < | 0.1 | eV) as has been found for most other atoms and molecules\textsuperscript{50-52}. Vibrational structure is apparent for the process He\#(2\textsuperscript{3}S)/(CN)\textsubscript{2}\textsuperscript{+}(X 2Π\textsubscript{g}). It is found that, within experimental error, the vibrational spacings are the same for both modes of ionization. In comparing the vibrational envelope of the ground state ion for the two modes of ionization, differences are noted. This anomaly might be explained by a competing autoionization process\textsuperscript{51} as was suggested for the process He\#(2\textsuperscript{3}S)/O\textsubscript{2}\textsuperscript{+}(X 2Π\textsubscript{g}). The photoionization-yield data of Dibeler and Liston\textsuperscript{129} for dicyanogen suggest that there may be an autoionizing state at approximately 19.8 eV. Thus, it may be possible to excite the dicyanogen molecule to this autoionizing level by resonant excitation transfer with He\#(2\textsuperscript{3}S) metastable atoms.
FIGURE 24. Electron spectra for the ionization of dicyanogen.
Table 15.

$\Delta E_{\text{obs}}$ energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*($2^3S$) Penning ionization of dicyanogen at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>$\Delta E_{\text{obs}}$ (eV)</th>
<th>Relative State Populations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>584 Å (21.22 eV)</td>
<td>He*($2^3S$) (19.82 eV)</td>
</tr>
<tr>
<td>X $^2\Pi_g$</td>
<td>-0.01 $\pm$ 0.03</td>
<td>100 $\pm$ 5</td>
</tr>
<tr>
<td>A $^2\Sigma^+_g$</td>
<td>-0.08 $\pm$ 0.03</td>
<td>63 $\pm$ 6</td>
</tr>
<tr>
<td>B $^2\Sigma^+_u$</td>
<td>-0.07 $\pm$ 0.03</td>
<td>30 $\pm$ 3</td>
</tr>
<tr>
<td>C $^2\Pi_u$</td>
<td>-0.02 $\pm$ 0.05</td>
<td>117 $\pm$ 6</td>
</tr>
</tbody>
</table>

a. Contains small contributions from He*($2^1S$) and He (584 Å).
For the normalized relative populations of electronic states for both He\(^{2}\!^{1}\!{S},^{2}\!^{3}\!{S}\) Penning ionization and 584 Å photoionization of (CN)\(_{2}\), relatively large differences are noted as shown in Table 15. It is observed that the partial ionization cross-section for the production of the \(\Pi\) states of (CN)\(_{2}\)\(^+\) relative to that for the \(\Sigma\) states is much smaller for Penning ionization than for photoionization.

There is some evidence to suggest that other types of chemi-ionization processes may also be occurring, since two unidentified peaks are observed at 1.8 eV and 0.7 eV. (This is beyond the energy range of Figure 24). These energies could correspond to autoionizing levels of (CN)\(_{2}\). The photoionization-yield curves for (CN)\(_{2}\) reported by Dibeler and Liston\(^{129}\) indicate the existence of autoionizing levels of (CN)\(_{2}\) which may be responsible for the observed bands but in this case some mechanism other than excitation transfer must be operative. For example\(^{50,133}\), some processes have been attributed to collisions with fast neutral helium atoms. It is possible that dissociative processes may also play an important role.

6.4. Acetonitrile.

Acetonitrile has the symmetry \(C_{3v}\) and ground state electron configuration\(^{134}\).

\[ .. (2a_1)^2 (3a_1)^2 (4a_1)^2 (2\!^{e})^4 (5\!a_1)^2 (3\!e)^4 ; 1\!A_1 \]

As described by Turner et al.\(^{132}\), the 3e orbital has \(C = N\) \(\Pi\) bonding, C-C bonding, and C-H antibonding character, the 5\!a_1
orbital has nitrogen lone pair bonding character, and the $2e$ orbital has C-C bonding, and C-H antibonding character.

In Figure 25, the $\text{He}^*(2^1S,2^3S)$ Penning electron and the 584 Å photoelectron spectra of CH$_3$CN are compared. Four states are observed in the photoelectron spectrum and these have been interpreted in previous studies$^{132,135}$. In the $\text{He}^*(2^1S,2^3S)$ Penning electron spectra four states are also observed. In Table 16, the $\Delta E_{\text{obs}}$ energy shift values are listed. There is some evidence for vibrational structure in the Penning spectrum for the ground state of the ion but as in the case of HCN no unique assignment of vibrational levels can be made. However, the tentative assignment (which assumes $\Delta E_A = 0$) shown in Figure 25, results in a small value of $\Delta E$ (-0.09 eV). Alternative assignments would result in much larger negative values of $\Delta E$. For the normalized relative populations of electronic states for both $\text{He}^*(2^1S,2^3S)$ Penning ionization and 584 0 Å photoionization of CH$_3$CN, relatively large differences are noted and are listed in Table 16. There is no evidence in the electron spectra for additional chemi-ionization processes of the type observed in dicyanogen.

6.5. Cyanogen Bromide and Cyanogen Iodide.

The ground state outer electron configuration of the cyanogen halides is$^{136}$

$$(1\sigma)^2 \ (2\sigma)^2 \ (3\sigma)^2 \ (1\Pi)^4 \ (4\sigma)^2 \ (2\Pi)^4 \ ; \ 1r^+$$

where the $3\sigma$ and $4\sigma$ orbitals are the lone pair orbitals on the halogen and nitrogen atoms. The $1\Pi$ and $2\Pi$ orbitals are
FIGURE 25. Electron spectra for the ionization of acetonitrile.
Table 16.

$\Delta E_{\text{obs}}$ energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*$(2^3S)$ Penning ionization of acetonitrile at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>$\Delta E_{\text{obs}}$ (eV)</th>
<th>Relative State Populations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>584 Å (21.22 eV)</td>
</tr>
<tr>
<td>$X^2E$</td>
<td>$-0.58 \pm .05$</td>
<td>100 $\pm$ 10</td>
</tr>
<tr>
<td>$A^2A_1$</td>
<td>$-0.30 \pm .03$</td>
<td>54 $\pm$ 5</td>
</tr>
<tr>
<td>$B^2E$</td>
<td>$-$</td>
<td>123 $\pm$ 24</td>
</tr>
<tr>
<td>$C^2A_1$</td>
<td>$-0.4 \pm .2$</td>
<td>39 $\pm$ 8</td>
</tr>
</tbody>
</table>

<sup>a</sup> Contains small contributions from He*$(2^1S)$ and He (584 Å).
respectively the in phase and out of phase combinations of the halogen p atomic orbital and the C = N \pi bond.

In Figure 26 and 27 the He*(2^1S,2^3S) Penning electron and the 584 Å photoelectron spectra of BrCN and ICN respectively are compared. The photoelectron spectra of these two molecules are very similar to those reported by Heilbronner et al.\textsuperscript{137} and also by Lake and Thompson\textsuperscript{138}, both of whom have given a similar interpretation of the spectra.

The four ionic states of BrCN observed in the photoelectron spectrum are also observed in the He*(2^1S,2^3S) Penning electron spectra (Figure 26). The \( \Delta E_{\text{obs}} \) energy shift values are listed in Table 17. For the ground state of BrCN\(^+\), \( \Delta E_{\text{obs}} = \Delta E \), on the basis of the assignment (which assumes \( \Delta E_A = 0 \)) shown in Figure 26. In addition, for this state although there is no resolution of vibrational structure, the two components of the spin-orbit coupling are partially resolved in the Penning electron spectra. It appears that partial cross-sections for He*(2^3S) Penning ionization to these two spin-orbit coupling components of BrCN\(^+\) may differ while for photoionization they appear to be approximately the same. The difference may be due to autoionization phenomena. A similar situation occurs in the Penning ionization of xenon\textsuperscript{50}.

The normalized relative populations of electronic states for both He*(2^3S) Penning ionization and 584 Å photoionization of BrCN are listed in Table 17 and large differences are noted.
FIGURE 26. Electron spectra for the ionization of cyanogen bromide.
FIGURE 27. Electron spectra for the ionization of cyanogen iodide.
Table 17.

$\Delta E_{\text{obs}}$ energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and $\text{He}^*(2^3S)$ Penning ionization of cyanogen bromide at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>$\Delta E_{\text{obs}}$ (eV)</th>
<th>Relative State Populations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{X}$ $^2\Pi_{\frac{3}{2},\frac{1}{2}}$</td>
<td>$-0.08^{a}\pm 0.07$</td>
<td>100 $\pm$ 5</td>
</tr>
<tr>
<td>$\bar{A}$ $^2\Sigma^+$</td>
<td>$-0.26^{a}\pm 0.03$</td>
<td>25 $\pm$ 1</td>
</tr>
<tr>
<td>$\bar{B}$ $^2\Pi_{\frac{3}{2},\frac{1}{2}}$</td>
<td>$-0.16^{a}\pm 0.05$</td>
<td>66 $\pm$ 3</td>
</tr>
<tr>
<td>$\bar{C}$ $^2\Sigma^+$</td>
<td>$-0.03^{a}\pm 0.05$</td>
<td>20 $\pm$ 1</td>
</tr>
</tbody>
</table>

a. An averaged value.

b. Contains small contributions from $\text{He}^*(2^1S)$ and He (584 Å).
For photoionization, the magnitude of the relative populations of electronic states are similar in the case of both \( \Sigma \) states and also in the case of both \( \Pi \) states but for Penning ionization the situation is different.

Finally the BrCN two unidentified peaks (I,II) are observed at 1.39 eV and 0.3 eV. It is suggested that these electrons could arise from the autoionization of excited fragments. This may involve an excited state of BrCN which predissociates and is then followed by autoionization of excited Br or CN. In a study of \( \text{Br}_2 \), Čermák\(^{133}\) has observed an autoionizing level for the bromine atom (6p') which may correspond to the peak at 0.3 eV.

The four ionic states of ICN observed in the photoelectron spectrum are also observed in the Penning electron spectra (Figure 27). The \( \Delta E_{\text{obs}} \) energy shift values are listed in Table 18. For the ground state of ICN\(^+\) there is evidence of vibrational structure in the Penning spectra for both components of the spin-orbit coupling. The spin-orbit splitting is found to be the same for the two modes of ionization. For the ground state of ICN\(^+\), \( \Delta E_{\text{obs}} = \Delta E \), (assuming \( \Delta E_A = 0 \)). Significant differences are observed in comparing the shapes of the vibrational envelopes for the two spin-orbit coupling components of the ground state of ICN\(^+\) for Penning ionization and photoionization. Autoionization is an unlikely reason for this difference since suitable bands are not observed in the photoionization-efficiency curves of ICN\(^{129}\). It appears that the partial cross-section for \( \text{He}^*(2^3S) \) Penning ionization to the two spin-orbit...
Table 18.

$\Delta E_{\text{obs}}$ energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and $\text{He}^*(2^3S)$ Penning ionization of cyanogen iodide at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>$\Delta E_{\text{obs}}$ (eV)</th>
<th>Relative State Populations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>584 Å (21.22 eV)</td>
</tr>
<tr>
<td>$\bar{X} \bar{\Pi}^{1/2} \bar{\Sigma}^{3/2}$</td>
<td>-0.01 ± 0.04</td>
<td>100 ± 5</td>
</tr>
<tr>
<td>$\bar{A} \bar{2} \Sigma^+$</td>
<td>-0.26 ± 0.03</td>
<td>34 ± 3</td>
</tr>
<tr>
<td>$\bar{B} \bar{2} \Pi^{1/2} \bar{\Sigma}^{3/2}$</td>
<td></td>
<td>78 ± 8</td>
</tr>
<tr>
<td>$\bar{C} \bar{2} \Sigma^+$</td>
<td>-0.42 ± 0.05</td>
<td>26 ± 1</td>
</tr>
</tbody>
</table>

a. An averaged value for the spin-orbit components.
b. Contains small contributions from $\text{He}^*(2^1S)$ and $\text{He}^*(584 \text{ Å})$. 
coupling components of ICN⁺ are approximately the same as is observed for photoionization.

The normalized relative populations of electronic states for both He*(2⁢S) Penning ionization and 584 Å photoionization of ICN are listed in Table 18. It was not possible to deconvolute the bands due to the \( \bar{A} \ 2\Sigma^+ \) or \( \bar{B} \ 2\Pi_{\frac{3}{2},\frac{1}{2}} \) states in the He*(2⁢S) Penning electron spectra so they are reported as a combined value. For ICN the data for the two modes of ionization are of the same magnitude and trend as was observed for BrCN. No data was included for the process He*(2⁢S)/ICN⁺ (\( \bar{C} \ 2\Sigma^+ \)) because the full width at the half peak height of the Penning electron structure is approximately three times larger than would be expected from a consideration of the photoelectron spectrum. This suggests that other chemi-ionization processes may be contributing to this peak as well as the two unidentified peaks (labeled I,II). It is suggested that these electrons may arise from the autoionization of excited fragments.
CHAPTER SEVEN

WATER, ALCOHOLS AND ETHERS

7.1. Introduction.

Using a retarding potential electron spectrometer of low resolution, Čermák has studied the Penning electron spectrum of H$_2$O using both He*(2$^1$S,2$^3$S) and Ne*(3$^1$P,3$^3$P$_2$) metastables. Čermák has also studied the Penning electron spectra of methanol, ethanol, dimethyl ether and ethylene oxide using Ne*(3$^1$P,3$^3$P$_2$) metastables. Only qualitative interpretations of these spectra are possible due to the limited resolution available. More recently, Čermák has studied the Penning ionization to the first band of ethylene oxide using Ar*(3$^1$P,3$^3$P$_2$) metastable atoms at higher electron energy resolution. In this chapter the He*(2$^1$S,2$^3$S) Penning ionization of water, alcohols and ethers are reported and the results are compared to the corresponding 584 Å photoelectron spectra.

7.2. Water.

The water molecule belongs to the point group C$_{2v}$ and has the ground state electron configuration.

$$ (1a_1)^2 \ (2a_1)^2 \ (1b_2)^2 \ (3a_1)^2 \ (1b_1)^2 \ ; \ \ ^1A_1 $$

The $1b_1$ orbital is essentially the oxygen lone pair ($2p_x$) which is perpendicular to the molecular plane. The $3a_1$ orbital includes H-H bonding character while the $1b_2$ involves H-H antibonding character.$^{132}$
In Figure 28, the He*(2\textsuperscript{1}S,2\textsuperscript{3}S) Penning electron and the 584 Å photoelectron spectra of water are compared. The 584 Å photoelectron spectrum is similar to that reported by Turner\textsuperscript{132}. The vibrational spacings for the $\tilde{X} \text{2B}_1$ electronic state of H\textsubscript{2}O\textsuperscript{+} formed in the photoionization process are indicated in Figure 28.

In the upper portion of Figure 28, the Penning spectrum reveals structure for the He*(2\textsuperscript{3}S)/H\textsubscript{2}O\textsuperscript{+}(X \text{2B}_1) and the He*(2\textsuperscript{3}S)/H\textsubscript{2}O\textsuperscript{+} (A \text{2A}_1) processes. Using the background subtraction technique\textsuperscript{52}, the region where quantitative analysis is possible is extended down to 0.75 eV, as shown in the central portion of Figure 28.

In addition to the X \text{2B}_1 and the A \text{2A}_1 bands in the Penning electron spectrum, part of the B \text{2B}_2 band can also be observed. It appears that Penning ionization is predominantly due to He*(2\textsuperscript{3}S) metastables and for the X \text{2B}_1 state it is estimated that approximately 5\% of the total band area is due to He*(2\textsuperscript{1}S) metastables.

Large $\Delta E_{\text{obs}}$ energy shift values (Table 19) are observed for the processes He*(2\textsuperscript{3}S)/H\textsubscript{2}O\textsuperscript{+}(X \text{2B}_1) and He*(2\textsuperscript{3}S)/H\textsubscript{2}O\textsuperscript{+}(A \text{2A}_1). No value is indicated for the He*(2\textsuperscript{3}S)/H\textsubscript{2}O\textsuperscript{+}(B \text{2B}_2) process since the full band is not observed. The first band labelled 2\textsuperscript{3}S(X \text{2B}_1) in the Penning electron spectrum exhibits partially resolved vibrational structure. A tentative assignment for the He*(2\textsuperscript{3}S)/H\textsubscript{2}O\textsuperscript{+}(X \text{2B}_1) process (assuming $\Delta E_A = 0$) is illustrated in Figure 28 and places the (1,0,0) vibration at the peak maximum. This corresponds to a $\Delta E$ energy shift of +0.040 eV which is of the same
FIGURE 28. Electron spectra for the ionization of water.
Table 19.

\( \Delta E_{\text{obs}} \) energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*\(^{(2\,S)}\) Penning ionization of water at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>( \Delta E_{\text{obs}} ) (eV)</th>
<th>Relative State Populations</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X^2B_1 )</td>
<td>(-0.37 \pm 0.03)</td>
<td>95 ( \pm 5 )</td>
</tr>
<tr>
<td>( A^2A_1 )</td>
<td>(-0.43 \pm 0.08)</td>
<td>100 ( \pm 5 )</td>
</tr>
<tr>
<td>( B^2B_2 )</td>
<td></td>
<td>83 ( \pm 8 )</td>
</tr>
</tbody>
</table>

\(^a\) Contains small contributions from He*\(^{(2\,S)}\) and He (584 Å).
magnitude as observed for atoms\textsuperscript{50} and most molecules\textsuperscript{51-53} previously studied with helium metastables. It is difficult to rationalize any alternative vibrational assignments for this band. A discussion of the apparent differences of the Franck-Condon factors for photoionization and Penning ionization to the ground state ion of H\textsubscript{2}O and the other molecules reported in this section is given at the end of this chapter.

For the normalized relative populations of electronic states for He\textsuperscript{*}(2\textsuperscript{1}S,2\textsuperscript{3}S) Penning ionization and 584 Å photoionization of H\textsubscript{2}O, relatively large differences are observed and listed in Table 19. Since the He\textsuperscript{*}(2\textsuperscript{1}S) metastables contribute less than 10\% of the total structure in the Penning spectrum, the data for the normalized relative population is essentially that for ionization by He\textsuperscript{*}(2\textsuperscript{3}S) metastables. Previously\textsuperscript{51} it has been suggested that the difference in "impact" energies for the two modes of ionization might explain the observed differences for the normalized relative population of electronic states. Branton and Brion\textsuperscript{95} have measured the energy dependance of the partial cross-sections for the "photoionization" of H\textsubscript{2}O and this data shows that the ratio of partial cross-sections, $X^2B_1/\bar{X}^2A_1$, decreases as the photoionization energy decreases in the energy range of 21.2 eV to 19.8 eV. This trend is in agreement with the data for the normalized relative populations for the two states $X^2B_1$ and $\bar{X}^2A_1$ as shown in Table 19.
7.3. Methanol and Ethanol.

Methanol [CH\textsubscript{3}OH] belongs to the point group C\textsubscript{s} and has the ground state electron configuration\textsuperscript{140}.

\[(1\alpha')^2 (2\alpha')^2 (3\alpha')^2 (4\alpha')^2 (5\alpha')^2 (6\alpha')^2 (7\alpha')^2; 1A'\]

The molecular orbitals 2α" and 7α' are essentially the 2p\textsubscript{π} orbitals of oxygen while the 1α" and the 5α' are essentially the 2p\textsubscript{π} orbitals of the methyl group\textsuperscript{140}.

Ethanol [C\textsubscript{2}H\textsubscript{5}OH] has the ground state outer electron configuration

\[\ldots(\psi\textsubscript{4})\textsuperscript{m} (\psi\textsubscript{3})\textsuperscript{n} (\alpha')^2 (\alpha'')^2; 1A'\]

Since the symmetry of the molecular orbitals is unknown, \(\psi\textsubscript{4}\) designates the \(l\)th highest filled molecular orbital.

In Figures 29 and 30 the He\#(2\textsuperscript{1}S,2\textsuperscript{3}S) Penning electron spectra and the 584 Å photoelectron spectra of methanol and ethanol respectively are compared. The 584 Å photoelectron spectra are similar to those reported by Robin and Keubler\textsuperscript{140}. Using a low resolution electron analyzer, Čermák has observed some broad bands for Ne\#(3\textsuperscript{3}P\textsubscript{0},3\textsuperscript{3}P\textsubscript{2}) Penning ionization of methanol and ethanol\textsuperscript{28}.

In the top portion of Figure 29, four bands are observed for He\#(2\textsuperscript{1}S,2\textsuperscript{3}S) Penning ionization of methanol. It is likely that two states (\(\Xi + \overline{\Xi}\)) are contributing to the band with the peak maximum at 4.44 eV. In the top portion of Figure 30, six bands are observed for the He\#(2\textsuperscript{1}S,2\textsuperscript{3}S) Penning ionization of ethanol corresponding to the six observed bands in the 584 Å
Penning Ionization (He*2s,2s)

CH₃OH

2s(3A')

2s(3S)

2s(DA')

Spectrum & Background

Background Subtracted

Photoionization (584 Å)

Electron spectra for the ionization of methanol.
Penning Ionization (He*2'S, 2'S)

CH$_3$CH$_2$OH

Spectrum & Background
Background Subtracted

Photoionization (584 Å)

FIGURE 30. Electron spectra for the ionization of ethanol.
photoionization of ethanol. The central portions (background subtracted) of Figures 29 and 30 reveal regions extending down to \( \sim 1.0 \) eV where analysis is possible.

Large \( \Delta E_{\text{obs}} \) energy shifts are measured for methanol and are listed in Table 20. It appears (Figure 29) that relative to the partial cross-section for \( \text{He}^*(2^3S)/\text{CH}_3\text{OH}^+ (\tilde{B}^2A') \), the cross-section for \( \text{He}^*(2^3S)/\text{CH}_3\text{OH}^+ (\tilde{C}^2A'') \) is small since no shoulder is observed on the peak. The normalized relative populations of electronic states for both \( \text{He}^*(2^1S,2^3S) \) Penning ionization and 584 Å photoionization of methanol are listed in Table 20. Results are normalized with respect to the first electronic state (\( \tilde{X}^2A'' \)). Since the \( \tilde{B}^2A' \) and \( \tilde{C}^2A'' \) states are not resolved for either mode of ionization they were combined together when calculating the relative populations of the electronic states. In comparing the normalized relative populations for the two modes of ionization large differences are observed.

Large \( \Delta E_{\text{obs}} \) energy shifts also are measured for ethanol and are listed in Table 21. Below 26 eV, Robin and Keubler have predicted nine ionization potentials but observed only seven using 584 Å and 304 Å radiation. In the electron spectra shown in Figure 30, there is some evidence of structure for six bands. The normalized relative populations of electronic states for the two modes of ionization are listed in Table 21. Results are normalized with respect to the first electronic state (\( \tilde{X}^2A'' \)). In both the Penning electron spectra and the photoelectron spectrum the third and fourth states, labelled \( \tilde{B} \) and \( \tilde{C} \), are not resolved.
Table 20.

$\Delta E_{\text{obs}}$ energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*(2 $^3$S) Penning ionization of methanol at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>$\Delta E_{\text{obs}}$ (eV)</th>
<th>Relative State Populations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>584 Å (21.22 eV)</td>
</tr>
<tr>
<td>X $^2$A''</td>
<td>$-0.42 \pm 0.05$</td>
<td>100 $\pm$ 5</td>
</tr>
<tr>
<td>A $^2$A'</td>
<td>$-0.42 \pm 0.08$</td>
<td>99 $\pm$ 5</td>
</tr>
<tr>
<td>B $^2$A'</td>
<td>$-0.22 \pm 0.08$</td>
<td>211 $\pm$ 11</td>
</tr>
<tr>
<td>C $^2$A''</td>
<td></td>
<td>211 $\pm$ 11</td>
</tr>
<tr>
<td>D $^2$A''</td>
<td>$-0.15 \pm 0.10$</td>
<td>109 $\pm$ 6</td>
</tr>
</tbody>
</table>

\(^a\) Contains small contributions from He*(2 $^1$S) and He (584 Å).
Table 21.

$\Delta E_{\text{obs}}$ energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*($2^3$S) Penning ionization of ethanol at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>$\Delta E_{\text{obs}}$ (eV)</th>
<th>Relative State Populations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$584^0$ Å (21.22 eV)</td>
</tr>
<tr>
<td>$X^2\tilde{A}''$</td>
<td>$-0.47 \pm 0.08$</td>
<td>100 ± 10</td>
</tr>
<tr>
<td>$A^2\tilde{A}'$</td>
<td>$-0.37 \pm 0.10$</td>
<td>97 ± 15</td>
</tr>
<tr>
<td>$B$</td>
<td>$-0.55 \pm 0.10$</td>
<td></td>
</tr>
<tr>
<td>$C$</td>
<td></td>
<td>262 ± 50</td>
</tr>
<tr>
<td>$D$</td>
<td>$-0.23 \pm 0.10$</td>
<td>111 ± 21</td>
</tr>
<tr>
<td>$E$</td>
<td>$-0.26 \pm 0.10$</td>
<td>82 ± 12</td>
</tr>
</tbody>
</table>

$^a$ Contains small contributions from He*($2^1$S) and He (584 Å).
and so a combined value is given for the relative populations of the electronic states. In comparing the normalized relative populations for the two modes of ionization, large differences are observed.

### 7.4. Isopropyl Alcohol and Tertiary Butyl Alcohol

Both isopropyl alcohol \([(CH_3)_2CHOH]\) and t-butyl alcohol \([(CH_3)_3COH]\) have outer electron configurations of the type 

\[ (\psi_4)^m (\psi_3)^n (a')^2 (a'')^2 \; ; \; ^1A' \]

Since the symmetry of the molecular orbitals is unknown, \(\psi_4\) designates the \(i^{th}\) highest filled molecular orbital.

In Figures 31 and 32 the \(He^*(2^1S, 2^3S)\) Penning spectra and the 584 Å photoelectron spectra of isopropyl alcohol and t-butyl alcohol are shown. The 584 Å photoelectron spectra are similar to those reported by Robin and Kuebler\(^{140}\). The complex, broad and overlapping bands in the electron spectra of both alcohols preclude any unequivocal assignment of the bands in the Penning spectra, except for the ground states of the ions. The \(AE_{obs}\) values for the ground state of isopropyl alcohol and t-butyl alcohol are \(-0.41 \pm 0.10\) eV and \(-0.49 \pm 0.10\) eV respectively.

### 7.5. Dimethyl Ether and Ethylene Oxide

Both dimethyl ether \([CH_3OCH_3]\) and the alicyclic analogue, ethylene oxide \([CH_2OCH_2]\), have the symmetry \(C_{2v}\). The ground state electron configuration of dimethyl ether is\(^{141}\).

\[(1a_1)^2 (2a_1)^b (1b_2)^2 (CH bonding)^{12} (2b_2)^2 (3a_1)^2 (1b_1)^2; ^1A\]
FIGURE 31. Electron spectra for the ionization of isopropyl alcohol.
FIGURE 32. Electron spectra for the ionization of tertiary butyl alcohol.
The effective degeneracy of the C-H bonding is removed due to an interaction with another orbital, probably the 2b_2 (C-O bonding) orbital.

The ground state electron configuration of ethylene oxide is

...(2b_1)^2 (1b_2)^2 (5a_1)^2 (1a_2)^2 (3b_1)^2 (6a_1)^2 (2b_2)^2 ; ^1A_1

The 1b_2, 1a_2 and 2b_2 are \pi orbitals.

In Figures 33 and 34, the He*(2^1S, 2^3S) Penning electron spectrum and the 584 Å photoelectron spectrum of dimethyl ether and ethylene oxide respectively are compared. The 584 Å photoelectron spectrum of dimethyl ether (Figure 33) shows five ionic states as reported by Cradock and Whiteford. The 584 Å photoelectron spectrum of ethylene oxide (Figure 34) reveals four bands composed of six ionic states and is very similar to that reported by Basch et al. Some nitrogen impurity is observed and is labelled as such in Figure 34. Using Ne*(3^3P_0, 3^3P_2) metastable atoms, Čermák has observed three broad bands for the Penning ionization of both dimethyl ether and ethylene oxide. In the upper portion of Figure 33 at least four bands, corresponding to the states \tilde{X} ^2B_1, \tilde{A} ^2A_1, \tilde{C} and \tilde{D}, are observed for the He*(2^3S) Penning ionization of dimethyl ether. The third band may also contain an unresolved contribution from the \tilde{B} ^2B_2 state. In the upper portion of Figure 34 only four bands are observed for the He*(2^3S) Penning ionization of ethylene oxide. For both of these molecules the ratio of He*(2^1S) to He*(2^3S) Penning ionization to the ground state of the ion is somewhat larger.
FIGURE 33. Electron spectra for the ionization of dimethyl ether.
Penning Ionization ($\text{He}^*2\Sigma^+$)

$2^3\Sigma(B_1)$  $2^3\Pi(A_1)$

Spectrum & Background

Background Subtracted

Photoionization (584 Å)

FIGURE 34. Electron spectra for the ionization of ethylene oxide.
than has been observed for most of the other molecules studied in this series.

The $\Delta E_{\text{obs}}$ energy shifts are measured for dimethyl ether and are listed in Table 22 together with the normalized relative populations of electronic states for both He*(2$^1$S,2$^3$S) Penning ionization and 584 Å photoionization. Results are normalized with respect to the $X^2B_1$ electronic state. Since the $\tilde{E}$ and $\tilde{C}$ states are not resolved in either mode of ionization, a combined value is given for the relative population of these electronic states. In comparing the normalized relative populations for the two modes of ionization large differences are observed.

The $\Delta E_{\text{obs}}$ energy shifts are also measured for ethylene oxide and are listed in Table 23 together with the normalized relative populations of electronic states for both He*(2$^1$S,2$^3$S) Penning ionization and 584 Å photoionization. Results are normalized with respect to the $X^2B_2$ electronic state. In the electron spectrum there are two unresolved pairs of ionic states ($\tilde{E} + \tilde{C}$) and ($\tilde{D} + \tilde{E}$) and therefore a combined value for the relative state populations in each case is given in Table 23. Large differences are observed in comparing the normalized relative populations for the two modes of ionization.

### 7.6. Diethyl Ether, Tetrahydrofuran and 1,4 Dioxane.

Diethyl ether [C$_2$H$_5$OC$_2$H$_5$] and the alicyclic analogue, tetrahydrofuran [CH$_2$CH$_2$OCH$_2$CH$_2$], can both be considered as belonging to the point group C$_{2v}$ and to have a ground state outer
Table 22.

$\Delta E_{\text{obs}}$ energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*(2^3S) Penning ionization of dimethyl ether at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>$\Delta E_{\text{obs}}$ (eV)</th>
<th>Relative State Populations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>584 Å (21.22 eV)</td>
</tr>
<tr>
<td>$\tilde{X}^2B_1$</td>
<td>-0.34 ± 0.05</td>
<td>100 ± 10</td>
</tr>
<tr>
<td>$\tilde{A}^2A_1$</td>
<td>-0.35 ± 0.08</td>
<td>77 ± 8</td>
</tr>
<tr>
<td>$\tilde{B}^2B_2$</td>
<td></td>
<td>223 ± 22</td>
</tr>
<tr>
<td>$\tilde{C}(\text{CH bonding})$</td>
<td>-0.1 ± 0.1</td>
<td>218 ± 22</td>
</tr>
<tr>
<td>$\tilde{D}(\text{CH bonding})$</td>
<td>-0.16 ± 0.10</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Contains small contributions from He*(2^1S) and He (584 Å).
Table 23.

\( \Delta E_{\text{obs}} \) energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He\(^*(2^3S)\) Penning ionization of ethylene oxide at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>( \Delta E_{\text{obs}} ) (eV)</th>
<th>Relative State Populations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>584 Å (21.22 eV)</td>
</tr>
<tr>
<td>(-^2X) B(_2)</td>
<td>-0.35 ± 0.05</td>
<td>100 ± 5</td>
</tr>
<tr>
<td>(-^2) A(_1)</td>
<td>-0.45 ± 0.10</td>
<td>87 ± 4</td>
</tr>
<tr>
<td>(-^2B) B(_1)</td>
<td>-0.43 ± 0.10</td>
<td>201 ± 15</td>
</tr>
<tr>
<td>(-^2) C(_2) A(_2)</td>
<td>—</td>
<td>229 ± 30</td>
</tr>
</tbody>
</table>

\(^a\) Contains small contributions from He\(^*(2^1S)\) and He (584 Å).
electron configuration of the type

\[ \ldots (\psi_4)^m (\psi_3)^n (a_1)^2 (b_1)^2 \quad ; \quad 1A_1 \]

Since the symmetry of the molecular orbitals is unknown, \( \psi_k \) designates the \( k \)th highest filled molecular orbital.

In Figures 35 and 36 the He\(^*(2^1S, 2^3S)\) Penning electron spectra and the 584 Å photoelectron spectra of diethyl ether and tetrahydrofuran respectively are compared. Since the photoelectron spectra of these molecules have not previously been reported, the absolute energy scales are calibrated using both argon and nitrogen. For both molecules the photoelectron and the Penning electron spectra consist of a large number of overlapping bands.

1,4-dioxane \([\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2]\) has the symmetry \( C_{2h} \) and has the ground state outer electron configuration

\[ \ldots (\psi_4)^m (\psi_3)^n (1b_g)^2 (1a_g)^2 (2a_g)^2 \quad ; \quad 1A_g \]

where \( \psi_k \) designates the \( k \)th highest filled molecular orbital. In Figure 37 the He\(^*(2^3S)\) Penning electron spectrum of 1,4-dioxane is compared to the 584 Å photoelectron spectrum. The photoelectron spectrum is very similar to that reported by Kobayashi and Nagakura\(^{143}\). A large number of the states observed in the photoelectron spectrum are also observed in the Penning electron spectra.

The \( \Delta E_{\text{obs}} \) energy shifts for the three molecules are listed in Table 24. Quantitative measurements of the relative populations of electronic states are not obtained due to the
FIGURE 35. Electron spectra for the ionization of diethyl ether.
FIGURE 36. Electron spectra for the ionization of tetrahydrofuran.
FIGURE 37. Electron spectra for the ionization of 1,4 dioxane.
Table 24.

$\Delta E_{\text{obs}}$ energy shift in eV for He*(2$^3$S) Penning ionization of diethyl ether, tetrahydrofuran and 1,4 dioxane at 300 °K.

<table>
<thead>
<tr>
<th></th>
<th>Diethyl Ether</th>
<th>Tetrahydrofuran</th>
<th>1,4 Dioxane</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electronic State</strong></td>
<td><strong>$\Delta E_{\text{obs}}$ (eV)</strong></td>
<td><strong>$\Delta E_{\text{obs}}$ (eV)</strong></td>
<td><strong>$\Delta E_{\text{obs}}$ (eV)</strong></td>
</tr>
<tr>
<td>$\bar{X}$ $^2$ $B_1$</td>
<td>-0.17 ± 0.08</td>
<td>$\bar{X}$ $^2$ $B_1$</td>
<td>-0.33 ± 0.10</td>
</tr>
<tr>
<td>$Z$</td>
<td>-0.08 ± 0.10</td>
<td>$Z$</td>
<td>-0.29</td>
</tr>
</tbody>
</table>

- a. Averaged value.
large number of overlapping bands. However, a visual estimate with reference to the ground ionic state indicates large differences. For example, the second band of states in the spectra of these three molecules shows very significant differences between the two modes of ionization. This is particularly obvious in the case of 1,4-dioxane where the ratio, $A/B$, of cross-sections is much larger for photoionization. In addition, for all three molecules the intensity ratio, $X/Z$, where $Z$ refers to the last band, is very different for the two modes of ionization.

7.7. Discussion of the Franck-Condon Envelopes for Transitions to the Ground Ionic State.

In Figure 38 the He*(2^3S) Penning electron and 584 Å photoelectron spectra are shown for the ground ionic states of water, alcohols, ethers and related compounds. The $\Delta E_{\text{obs}}$ energy shifts, which are large (negative) for all molecules, are shown below the respective Penning spectra. The magnitude of these shifts can be visualized by a comparison with the energy scale shown in the photoelectron spectrum of water. It can be seen in all cases that, with respect to the photoelectron spectrum, the high energy side (left hand side) of the Penning electron peak is significantly asymmetric. This asymmetry is even more prominent when the rising background is taken into account. For a number of molecules there is evidence of vibrational structure in the Penning electron band. The Penning spectra have been positioned below the photoelectron spectra such that the
FIGURE 38. Electron spectra for the ground ionic states of water, alcohols, and ethers. Energy shifts are given in eV.
tentative vibrational assignment for the Penning band ($\Delta E_A = 0$) corresponds to that for photoionization. The broken markers indicate where vibrational structure might be expected. This vibrational assignment of the Penning spectra results in small $\Delta E$ values (shown on Figure 38) which are of the order of thermal energies as has been observed for most other molecules\textsuperscript{45,51,53}. Alternative assignments would result in large $\Delta E$ values of the order of one or more vibrational quanta. If these assignments are correct then the results suggest that there are large differences in the Franck-Condon factors for the two modes of ionization of these molecules. For Penning ionization this would imply that the target potential energy surfaces are modified by the influence of the helium particle. Even a small perturbation of the potential surface could result in significant changes in the Franck-Condon factors as discussed in a previous chapter. Alternatively these large differences in Franck-Condon factors might also be due to competing autoionization processes in which the autoionizing state is formed by resonant charge transfer with the helium metastable. This means, if a competing autoionization process is to explain the change in the Franck-Condon envelope, there would have to be an autoionizing level at 19.82 eV for the whole series of molecules studied and this seems unlikely. Furthermore, Čermák\textsuperscript{139} has also observed a difference in shape for Ar*($^3P_0,^3P_2$) Penning ionization of ethylene oxide and invoking the autoionization argument would require that there be two autoionizing levels in ethylene oxide which are resonant with the helium and the argon metastable atoms respectively.
CHAPTER EIGHT

CARBONYL CONTAINING COMPOUNDS

8.1. Introduction.

In this chapter the $\text{He}^*(2^1S,2^3S)$ Penning ionization of, HCHO, CH$_3$CHO, CH$_3$COCH$_3$, HCOOH and CH$_3$COOH, are reported. The $\text{He}^*(2^1S,2^3S)$ Penning ionization process is compared to that of 584 Å photoionization. High resolution photoelectron spectra of these five carbonyl-containing molecules have been reported in the literature. Using $\text{Ne}^*(3^1P_0,3^3P_2)$ metastables, Čermák has obtained a low resolution Penning electron spectrum of acetone but the Penning ionization of the other molecules has not been studied previously.

8.2. Formaldehyde and Acetaldehyde.

Formaldehyde [HCHO] has the symmetry $C_{2v}$ and the ground state electron configuration$^{144}$.

$$\ldots (1b_2)^2 (5a_1)^2 (1b_1)^2 (2b_2)^2 \; ; \; 1^A_1$$

where the $2b_2$ orbital is the oxygen non-bonding orbital and the $1b_1$ orbital is the C=O $\pi$-bonding orbital.

Acetaldehyde [CH$_3$CHO] has the symmetry $C_s$ and the ground state electron configuration$^{145}$.

$$\ldots (7a')^2 (1a'')^2 (8a')^2 (9a')^2 (2a'')^2 (10a')^2 \; ; \; 1^A_1$$

where the $10a'$ orbital is the oxygen non-bonding orbital and $2a''$ orbital is the C = O $\pi$-bonding orbital.
In Figures 39 and 40, the $\text{He}^*(2^1S, 2^3S)$ Penning electron and the 584 Å photoelectron spectra of formaldehyde and acetaldehyde respectively are compared. The 584 Å photoelectron spectrum of formaldehyde which contains three bands, is similar to that reported by Baker et al.\textsuperscript{123}. The third band contains contributions from both the $\bar{B}^2B_2$ and the $\bar{C}^2A_1$ states. In the upper portion of Figure 39, the same three bands observed in the photoelectron spectrum are also observed in the $\text{He}^*(2^1S, 2^3S)$ Penning electron spectrum. It appears that Penning ionization is predominately due to $\text{He}^*(2^3S)$ metastables however, there are traces of structure due to $\text{He}^*(2^1S)$ metastables and "internal" 584 Å photons\textsuperscript{49}. Recently, this laboratory reported the photoelectron spectrum of acetaldehyde\textsuperscript{146} and the ionization potentials are in good agreement with values reported by Meek et al.\textsuperscript{147}. In Figure 40, three of the five bands in the photoelectron spectrum of acetaldehyde show evidence of vibration structure. In the upper portion of Figure 40, five bands are also observed in the $\text{He}^*(2^1S, 2^3S)$ Penning electron spectrum of acetaldehyde.

The $\Delta E_{\text{obs}}$ energy shift values\textsuperscript{54} of formaldehyde are listed in Table 25. The first band, labelled $2^3S(\bar{X}^2B_2)$, in the Penning electron spectrum (Figure 39) has a vibrational envelope different from that in the first band in the photoelectron spectrum. A tentative assignment for the $\text{He}^*(2^3S)/\text{HCHO}^+(\bar{X}^2B_2)$ process, where $\Delta E_A$ is assumed to be zero\textsuperscript{54}, is illustrated in Figure 39 and places $v' = 1$ (for either the C=O stretch or the H-C-H deformation) at the peak maximum. This corresponds to a
FIGURE 39. Electron spectra for the ionization of formaldehyde.
FIGURE 40. Electron spectra for the ionization of acetaldehyde.
Table 25.

$\Delta E_{\text{obs}}$ energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He*$(2^3S)$ Penning ionization of formaldehyde at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>$\Delta E_{\text{obs}}$ (eV)</th>
<th>Relative State Populations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>584 Å (21.22 eV)</td>
</tr>
<tr>
<td>$X^2B_2$</td>
<td>-0.21 ± 0.05</td>
<td>100 ± 10</td>
</tr>
<tr>
<td>$A^2B_1$</td>
<td>-0.09 ± 0.10</td>
<td>100 ± 10</td>
</tr>
<tr>
<td>$B^2B_2$</td>
<td>-0.26 ± 0.08</td>
<td>410 ± 41</td>
</tr>
<tr>
<td>$C^2A_1$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. Contains small contributions from He*$(2^1S)$ and He (584 Å).
AE energy shift of -0.02 eV. A discussion of the apparent differences of the Franck-Condon factors for Penning ionization and photoionization to the ground state ion of HCHO and the other molecules is given at the end of this chapter. The $\Delta E_{\text{obs}}$ energy shift values measured for acetaldehyde are listed in Table 26.

The normalized relative populations of electronic states for $\text{He}^*(2^1S,2^3S)$ Penning ionization and 584 Å photoionization of formaldehyde and acetaldehyde respectively are listed in Tables 25 and 26. The $B^2B_2$ and the $C^2A_1$ states of formaldehyde are combined since they are not resolved in the electron spectra. In comparing the electronic state populations for the two modes of ionization, relatively small differences are observed for the two molecules. It is also noted that for the two molecules, the ratio of the relative electronic state populations for the $\bar{A}$ state (which corresponds to the removal of a C=O π-bonding electron) to the $\bar{X}$ state (which corresponds to the removal of the oxygen non-bonding electron) are very similar for Penning ionization and photoionization. This behaviour is different from that observed in the case of -C≡N containing molecules$^{55}$ and CO$^{51}$.

8.3. Acetone.

Acetone $[\text{CH}_3\text{COCH}_3]$ has the symmetry $C_{2v}$ and the ground state electron configuration$^{145}$.

$$...(3b_2)^2 (1b_1)^2 (7a_1)^2 (1a_2)^2 (4b_2)^2 (8a_1)^2 (2b_1)^2 (5b_2)^2;^1A_1$$

where the $5b_2$ orbital is essentially the oxygen non-bonding orbital and the $2b_1$ orbital is the C=O π-bonding orbital.
Table 26.  
$\Delta E_{\text{obs}}$ energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and $\text{He}^*(2^3S)$ Penning ionization of acetaldehyde at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>$\Delta E_{\text{obs}}$ (eV)</th>
<th>Relative State Populations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>584 Å (21.22 eV)</td>
</tr>
<tr>
<td>$X^2A'$</td>
<td>-0.31 ± 0.05</td>
<td>100 ± 5</td>
</tr>
<tr>
<td>$A^2A''$</td>
<td>-0.19 ± 0.10</td>
<td>113 ± 22</td>
</tr>
<tr>
<td>$B^2A'$</td>
<td>-0.48 ± 0.10</td>
<td>175 ± 35</td>
</tr>
<tr>
<td>$C^2A'$</td>
<td>-0.30 ± 0.10</td>
<td>287 ± 57</td>
</tr>
<tr>
<td>$D^2A''$</td>
<td>-0.26 ± 0.10</td>
<td>130 ± 26</td>
</tr>
</tbody>
</table>

a. Contains small contributions from $\text{He}^*(2^1S)$ and He (584 Å).
In Figure 41, the $\text{He}^\ast(2^1S,2^3S)$ Penning electron and the 584 Å photoelectron spectra of acetone are compared. The 584 Å photoelectron spectrum of acetone is similar to that reported by Brundle et al.\textsuperscript{148}. The upper portion of Figure 41 shows that the Penning electron spectrum lacks some of the features observed in the photoelectron spectrum.

The $\Delta E_{\text{obs}}$ energy shift values of acetone are listed in Table 27. No values are listed for the $B$ and $D$ states of acetone since the position of the peak maximum cannot be located. The normalized relative populations of electronic states for $\text{He}^\ast(2^1S,2^3S)$ Penning ionization and 584 Å photoionization of acetone are also listed in Table 27. For acetone the states labelled $\bar{A}$, $B$, $C$ and $D$, have been combined since they are not resolved in the electron spectra. Therefore, it was not possible to compare quantitatively the ratio of the electronic state populations of the $\bar{A}^2B_1$ to the $\bar{X}^2B_2$ as was done for the two previous molecules. A visual comparison suggests that relative to photoionization the ratio of the electronic states ($\bar{A}^2B_1/\bar{B}$) is much larger for Penning ionization.

8.4. Formic Acid and Acetic Acid.

Formic acid [HCOOH] has the symmetry $C_s$ and the ground state electron configuration\textsuperscript{149}.

$$...(8a')^2 (1a'')^2 (9a')^2 (2a'')^2 (10a')^2 ; \; ^1A_1$$

where the 10a' orbital is essentially the non-bonding $n_0$-orbital localized on the oxygen atoms and the 2a'' orbital is essentially the non-bonding antisymmetric $\pi_2$-orbital.
FIGURE 41. Electron spectra for the ionization of acetone.
Table 27.

$\Delta E_{\text{obs}}$ energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He$^\ast$(2 $^3$S) Penning ionization of acetone at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>$\Delta E_{\text{obs}}$ (eV)</th>
<th>Relative State Populations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>584 Å ($2^1 S$) (21.22 eV)</td>
</tr>
<tr>
<td>$X^2 B_2$</td>
<td>-0.31 ± 0.08</td>
<td>100 ± 10</td>
</tr>
<tr>
<td>$A^2 B_1$</td>
<td>+0.03 ± 0.10</td>
<td></td>
</tr>
<tr>
<td>$B$</td>
<td></td>
<td>664 ± 66</td>
</tr>
<tr>
<td>$C$</td>
<td>-0.27 ± 0.10</td>
<td></td>
</tr>
<tr>
<td>$D$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E$</td>
<td>-0.36 ± 0.10</td>
<td>331 ± 33</td>
</tr>
<tr>
<td>$F$</td>
<td>-0.26 ± 0.10</td>
<td>64 ± 64</td>
</tr>
</tbody>
</table>

$^a$ Contains small contribution from He$^\ast$(2 $^1$S) and He (584 Å).
Acetic acid \([\text{CH}_3\text{COOH}]\) has the symmetry \(C_s\). Following the photoelectron data of Sweigart and Turner\(^{150}\), acetic acid has the ground state outer electron configuration.

\[\ldots(\psi_m^m) (\psi_n^n) (1a'')^2 (1a')^2; \quad ^1A_1\]

Since the symmetry of the molecular orbitals is unknown, \(\psi_x\) designates the \(i\)th highest filled molecular orbital. The \(1a'\) orbital is essentially the non-bonding \(n_0\)-orbital and the \(1a''\) orbital is the non-bonding antisymmetric \(\pi_2\)-orbital.

In Figures 42 and 43 the He*\((2^1S,2^3S)\) Penning electron and the 584 Å photoelectron spectra of formic acid and acetic acid respectively are compared. The 584 Å photoelectron spectrum of formic acid (Figure 42) which contains five bands, is similar to those reported by Brundle et al.\(^{151}\) and Watanabe et al.\(^{152}\). In the upper portion of Figure 42 there is also evidence of five bands in the He*\((2^1S,2^3S)\) Penning electron spectrum. The vibrational structure observed in the photoelectron spectrum is not apparent in the Penning electron spectra. The 584 Å photoelectron spectrum of acetic acid (Figure 43) is similar to that reported by Sweigart and Turner\(^{150}\). In the upper portion of Figure 43 the same five bands observed in photoionization are also observed in Penning ionization.

The \(\Delta E_{\text{obs}}\) energy shift values of formic acid and acetic acid respectively are listed in Tables 28 and 29. No values are listed for the \(\overline{C}^2A''\) state of formic acid and the \(\overline{E}\) state of acetic acid because the positions of the respective peak maxima cannot be located. The normalized relative populations of
FIGURE 42. Electron spectra for the ionization of formic acid.
FIGURE 43. Electron spectra for the ionization of acetic acid.
Table 28.

ΔE_{obs} energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He^*(2^3S) Penning ionization of formic acid at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>ΔE_{obs} (eV)</th>
<th>584 Å (21.22 eV)</th>
<th>He(2^3S) (19.82 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X A'</td>
<td>-0.22 ± 0.08</td>
<td>100 ± 10</td>
<td>100 ± 10</td>
</tr>
<tr>
<td>A A''</td>
<td>-0.23 ± 0.08</td>
<td>119 ± 12</td>
<td>58 ± 6a</td>
</tr>
<tr>
<td>B A'</td>
<td>-0.17 ± 0.10</td>
<td>175 ± 25</td>
<td>258 ± 26a</td>
</tr>
<tr>
<td>C A''</td>
<td>-</td>
<td>88 ± 14</td>
<td></td>
</tr>
<tr>
<td>D A'</td>
<td>-0.14 ± 0.08</td>
<td>255 ± 26</td>
<td>292 ± 29a</td>
</tr>
</tbody>
</table>

a. Contains small contributions from He^*(2^1S) and He (584 Å).
Table 29.

$\Delta E_{\text{obs}}$ energy shift in eV and the normalized relative electronic state populations for 584 Å photoionization and He$^\#(2^3S)$ Penning ionization of acetic acid at 300 °K.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>$\Delta E_{\text{obs}}$ (eV)</th>
<th>584 Å (21.22 eV)</th>
<th>He$^#(2^3S)$ (19.82 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{X}^2A'$</td>
<td>-0.25 ± 0.08</td>
<td>100 ± 10</td>
<td>100 ± 10</td>
</tr>
<tr>
<td>$\text{A}^2A''$</td>
<td>-0.11 ± 0.08</td>
<td>118 ± 12</td>
<td>90 ± 9\textsuperscript{a}</td>
</tr>
<tr>
<td>$\text{B}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}$</td>
<td>-0.23 ± 0.10</td>
<td>576 ± 58</td>
<td>342 ± 34\textsuperscript{a}</td>
</tr>
<tr>
<td>$\text{D}$</td>
<td>-0.31 ± 0.10</td>
<td>339 ± 34</td>
<td>392 ± 39\textsuperscript{a}</td>
</tr>
<tr>
<td>$\text{E}$</td>
<td>-0.31 ± 0.88</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Contains small contributions from He$^\#(2^1S)$ and He (584 Å).
electronic states for He*(2^1S,2^3S) Penning ionization and 584 Å photoionization of formic acid and acetic acid are listed in Tables 28 and 29 respectively. The 2^2A' and the 2^2A" states of formic acid are combined since they are not resolved in the Penning electron spectra. A visual examination indicates that the ratio of the electronic state populations (2^2A'/2^2A") for He*(2^3S) Penning ionization is similar to that for 584 Å photoionization. For acetic acid, the pairs of states (2^2A' + 2^2C) and (2^2D + 2^2E) are combined since they are not resolved in the electron spectra. In comparing the electronic state populations for the two modes of ionization, differences are observed for the two molecules.

8.5. Discussion of the Franck-Condon Envelopes for Transitions to the Ground Ionic State.

In Figure 44 the He*(2^3S) Penning electron and 584 Å photoelectron spectra are shown for the ground ionic states of the aldehydes, acetone and the carboxylic acids. The ΔE_{obs} energy shifts which have been measured for these molecules are shown below the respective Penning electron spectra. The magnitude of these shifts can be visualized by a comparison with the energy scale shown in the photoelectron spectrum of acetic acid. It appears in all cases that the vibrational envelope observed for Penning ionization is different from that observed in photoionization. For acetaldehyde and acetone, there is evidence for vibrational structure in the Penning electron band. The Penning spectra are positioned below the photoelectron spectra such that the tentative vibrational assignment for the Penning band corresponds to that for photoionization. This
FIGURE 44. Electron spectra for the ground ionic state of some carbonyl containing compounds. Energy shifts are given in eV.
tentative vibrational assignment, which assumes $\Delta E_A$ is zero$^{54}$, results in small true $\Delta E$ values (as shown in Figure 44). These values are of the order of thermal energies as has been observed for other molecules$^{51-55}$. If the vibrational assignment is correct, the data suggest that there are significant differences in the Franck-Condon factors for the two modes of ionization of these molecules. This behaviour has been previously observed in a study of water, alcohols and ethers$^{54}$. This would imply that the target potential energy surfaces are appreciably modified by the presence of the helium particle. It has been shown that even a small perturbation of the potential surface could result in significant changes in the Franck-Condon factors$^{54}$. Large differences in Franck-Condon factors might also be caused by competing autoionization processes where the autoionizing state is formed by resonant charge transfer with the helium metastable. If a competing autoionization process is to explain the change in the Franck-Condon envelope, there would have to be an autoionizing level at 19.82 eV for the whole series of molecules studied and this seems unlikely.
CHAPTER NINE

CONCLUSIONS

Of the many commonly occurring chemi-ionization reactions which occur for the single collision process involving a long-lived neutral excited species and a neutral target molecule, Penning ionization appears to be the predominant reaction. Employing the techniques of electron spectroscopy, valuable information about the physics of the collision process has been obtained from the ejected Penning electron energy distributions of the various molecules studied.

From the results of this study, there appears to be a number of experiments which must be performed before the Penning ionization process is fully understood. From the previous discussions it is apparent that more information is required about how the electronic state populations of various molecules change as a function of photoionization energy. Additional information on the partial cross-sections for the various chemi-ionization reactions would also be useful. One technique which would provide some of this information is the relatively difficult experiment which would measure the electron energy distribution of a chemi-ionization electron in coincidence with the resulting ion. Finally, it is suggested that with the growing interest in solid state surfaces, the use of metastable atoms as surface sensitive probes may prove to be fruitful.
REFERENCES

BIBLIOGRAPHY


3. P.M. Penning, Naturwissenschaften, XV (1927) 818.


42. H. Hotop and A. Niehaus, Z. Physik, 228 (1969) 68.


PUBLICATIONS


