PHOTOCHEMIZATION IN CASES

by

A.J. Blake  B.Sc.(Hons.)

Department of Physics

A thesis
submitted for the degree of
Doctor of Philosophy
in the
University of Adelaide

August, 1966
## CONTENTS

Summary
Preface
Acknowledgements

**Chapter I. Review of the Processes of Photoionization**

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.1</td>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>I.2</td>
<td>Calculation of Photoionization Cross-Sections</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>I.2.1 The dipole approximation</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>I.2.2 The hydrogen atom</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>I.2.3 Approximations to other wavefunctions</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>I.2.4 Sua Rules</td>
<td>12</td>
</tr>
<tr>
<td>I.3</td>
<td>Atomic Photoionization Cross-sections</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>I.3.1 Comparison between experimental and theoretical cross-sections</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>I.3.2 Autoionization</td>
<td>16</td>
</tr>
<tr>
<td>I.4</td>
<td>Molecular Photoionization Cross-sections</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>I.4.1 Molecular spectra</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>I.4.2 The Frank-Condon principle</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>I.4.3 Ionization potentials of molecules</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>I.4.4 Threshold behaviour of ionization</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>I.4.5 Total photoionization cross-sections</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>I.4.6 Dissociative ionization</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>I.4.7 Thresholds of excited ionic states</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>I.4.8 Partial photoionization cross-sections</td>
<td>29</td>
</tr>
</tbody>
</table>
Chapter II. Measurement of Total Photoionization Cross-Sections

II.1 Light Sources for the Ultraviolet Region 33
II.2 Absorption Measurements 35
   II.2.1 Detectors for the ultraviolet region 35
   II.2.2 Procedure for measuring molecular oxygen absorption cross-sections 37
   II.2.3 Total absorption cross-sections for molecular oxygen in the region 1050 Å to 1250 Å 41
II.3 Photoionization Yield Measurements 42
   II.3.1 The single ion chamber method 43
   II.3.2 The double ion chamber method 44
   II.3.3 Intensity measurements in the ultraviolet region 45
   II.3.4 Procedure for measuring the total photoionization cross-section of nitric oxide 46
   II.3.5 Nitric oxide total photoionization cross-section in the 1150 Å to 1350 Å region 48

Chapter III. The Photoelectron Spectrometer

III.1 Introduction 51
III.2 Requirements of the Spectrometer 52
   III.2.1 Choice of spectrometer 53
III.3 Construction of the Apparatus 57
   III.3.1 The collimator 57
   III.3.2 The analysing grid and anode 58
III.3.3 Construction of the spectrometer  59
III.3.4 The vacuum chamber  60
III.3.5 The monochromator  61
III.4 Operation of the Spectrometer  62
   III.4.1 Electrode voltages  62
   III.4.2 Recording of the spectra  64
   III.4.3 Digital noise averaging  65
   III.4.4 Time constants of the apparatus  68
III.5 Performance of the Spectrometer  70
   III.5.1 The monoenergetic electron spectrum  70
   III.5.2 Factors effecting the resolution  73
   III.5.3 Calibration of the energy scale  75
   III.5.4 Electron collecting efficiency  76

Chapter IV. Partial photoionization cross-sections

IV.1 Molecular oxygen  79
   IV.1.1 Oxygen photoelectron energy spectra  79
   IV.1.2 Identification of the peaks  80
   IV.1.3 Unfolding the spectra  83
   IV.1.4 The partial photoionization cross-sections of oxygen  84
   IV.1.5 Variation of the partial photoionization cross-sections with wavelength  86
   IV.1.6 Autoionizing processes  89
IV.2 Molecular nitrogen

   IV.2.1 Photoelectron energy spectra of molecular nitrogen 94

   IV.2.2 Variation of the partial photionization cross-sections of molecular nitrogen with wavelength 95

IV.3 Water vapour

   IV.3.1 Photoelectron energy spectra of water vapour 96

   IV.3.2 Variation of the partial photionization cross-sections of water vapour with wavelength 98

Chapter V. Photoionization in the Atmosphere

V.1 Introduction 99

V.2 Photoelectrons in the ionosphere 100

   V.2.1 Calculation of the photoelectron energy distribution 101

   V.2.2 The primary photoelectron energy distribution 103

V.3 Fluorescence in the Ionosphere 106

   V.3.1 Fluorescent transitions 106

   V.3.2 Intensity of fluorescent emission 108

Chapter VI. Suggestions for further study of photoionization

VI.1 Future development of photoelectron spectroscopy 111

   VI.1.1 Improvements to the experimental technique 112

   VI.1.2 Further experiments 113

VI.2 Fluorescent radiation 116
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>VI.2.1</td>
<td>Radiation from fluorescent autoionization</td>
<td>116</td>
</tr>
<tr>
<td>Appendix I</td>
<td>Ultraviolet spectroscopy with a photoelectron spectrometer</td>
<td>129</td>
</tr>
<tr>
<td>Appendix II</td>
<td>Resolution of the analysing grid</td>
<td>121</td>
</tr>
<tr>
<td>Appendix III</td>
<td>Publications</td>
<td>125</td>
</tr>
<tr>
<td>Bibliography</td>
<td></td>
<td>126</td>
</tr>
</tbody>
</table>
This thesis describes the measurement of partial photoionisation cross-sections for processes which lead to the formation of the ion in a particular quantum state. Partial cross-sections for oxygen, nitrogen and water vapour have been measured.

Previous determinations of photoionization cross-sections have been limited to measurements of the total cross-section for a multiplicity of processes corresponding to transitions to any one of a number of quantum states of the ion. Two examples of total cross-section measurements are presented in this thesis. Total cross-sections of molecular oxygen have been measured in the region from 1050 Å to 1250 Å. This region includes the wavelength of hydrogen Lyman-α, an important emission line in the solar spectrum. A double parallel plate ion chamber has been used to measure total photoionization cross-sections of nitric oxide in the region 1150 Å to 1350 Å. This chamber has also been used with argon to measure absolute beam intensities according to the method of Samson.

The partial photoionization cross-sections have been determined by recording the energy spectra of the photo-electrons. The spectrometer, which was of the
retarding potential type, consisted of three concentric cylindrical electrodes: a collimating electrode, an analyzing grid, and an anode. A one-metre near normal incidence monochromator has been used with a slit width corresponding to a resolution of 10 Å. The monochromator has been equipped with a helium capillary discharge lamp powered by a condensed spark discharge.

Electron energy spectra have been recorded by differentiating the output of the electrometer which measured the electron current at the anode, and applying this signal and the retarding voltage to the Y and X axes respectively of an X-Y co-ordinate plotter. Smoothed spectra have been obtained by digitising the spectra and using the memory storage of a multichannel analyser to add several scans of the spectrum.

Interpretation of the spectra has been aided by a study of the spectra of argon and hydrogen, which contain a single line and a single band respectively in the range of wavelengths used. The peak in the argon spectrum had a width at half height of 0.4 eV under the best conditions.

Spectra have been obtained over a wavelength range from the threshold for the first excited state of the ion to 584 Å for oxygen, nitrogen and water vapour.
The relative area associated with each peak has been measured, and this information combined with the total photoionization cross-section data of Cook and Metzger to produce partial cross-sections.

The partial cross-sections of oxygen show the thresholds of the $b^3\Sigma^+_g$ and $a^3\Pi_u$ states of $O_2^+$; the $A^2\Pi_u$ and the $a^3\Pi_u$ states are not properly resolved. The continua are seen to have the form of a step function modified by competition between the continua, and by autoionizing processes. At wavelengths longer than the $a^3\Pi_u$ threshold the spectra have a large peak at low energy as well as the peak corresponding to the $2\Pi_g$ ground state. It is suggested that fluorescence occurs from a highly excited level of $O_2$ before autoionization to the $X^2\Pi_g$ state of $O_2^+$.

The nitrogen results show the thresholds of the $B^2\Pi_u^+$ and $A^2\Pi_u$ states of $N_2^+$. All the continua have a maximum just below the threshold. The $B^2\Sigma_u^+$ continuum has a maximum value which is less than half the maximum values of the $A^2\Pi_u$ and $X^2\Sigma_g^+$ continua.

The water vapour results show the continua corresponding to the $2\Sigma_A$ and $2\Pi_A$ levels of $H_2O^+$, and another corresponding to dissociative ionization. These continua have little structure, and the onset is more
gradual than in the case of oxygen and nitrogen.

The partial photoionization cross-sections have been used in calculations of the energy distribution of primary photoelectrons in the ionosphere, and in calculations of the overhead intensities of various fluorescent band systems emitted in the ionosphere.