PHOTOIONIZATION OF ATOMS AND MOLECULES
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PHOTOIONIZATION OF ATOMS AND MOLECULES

Fred L. Mohler
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Photoionization of Atoms and Molecules

by Fred L. Mohler*

This is a review of experimental results on photoionization of atoms and some molecules. There are some quantitative data on all the alkalies, magnesium, calcium and thallium and all rare gases except xenon. Results are given for the common gases; hydrogen, nitrogen, oxygen, CO, CO2, NO, N2O, NO2, H2O and CH4. Autoionization, excitation to a state above the ionization threshold followed by transition to the ionized state, can be an important factor. Often the broad autoionization lines mask the true continuum. There are some mass spectrometric measurements of photoionization products for most of these molecules.

1. INTRODUCTION

The purpose of this report is to give a survey and bibliography of experimental measurements of photoionization and of the continuous absorption bands resulting in photoionization. The scope of this report will include atoms and some simple diatomic and polyatomic molecules. A survey of this subject through 1955 is given in a Handbuch der Physik article by G. L. Weissler [1].

Ever since the publication of Bohr's theory of atomic structure it has been recognized that beyond each absorption series there will be a continuous absorption band arising from removal of an electron from the atom with kinetic energy. Characteristic X-ray absorption spectra are photoionization continua that have been quite systematically studied [2]. The absorption for each X-ray level begins abruptly at the series limit and decreases roughly as the cube of the wavelength \( \lambda \). A general formula for this absorption is

\[
\sigma_n = c_n Z^a \lambda^b
\]

where \( \sigma_n \) is the atomic absorption coefficient for each X-ray level \( K, L_1, L_2, L_3, M_1, M_2, \) etc., and \( c_n \) is a constant involving the quantum numbers of each X-ray level and the threshold wavelength of the level and \( Z \) is the atomic number. \( a \) is roughly 4 and \( b \) ranges from 2.5 to 3.

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In contrast to the X-ray range, the experimental data on photoionization of valence electrons remain to this day quite fragmentary and incomplete. The photoionization bands fall in general in the vacuum ultraviolet which involves serious experimental difficulties. Furthermore, there are relatively few elements that are monatomic in the gas phase. The rare gases are the only elements that are purely monatomic. Vapors of the electro-positive metals are predominantly monatomic, but in most cases diatomic molecules of relatively low stability have also been observed in the vapor [3].

The photoionization absorption is conveniently expressed in terms of the absorption per atom (the effective atomic collision area for the photon) here written as $\sigma$. It is also expressed as the absorption per cm, $\alpha$, in gas at normal pressure and temperature,

$$\sigma = \alpha \times 3.72 \times 10^{-20}.$$  

One can measure the absorption of a column of gas at a known pressure, or alternatively one can measure the ion current produced by a measured radiation flux [5,6] in gas at a known pressure. This alternative method can be used in metal vapors at pressures too low to give measurable absorption.

In most atoms there are excited states of the neutral atom which fall above the first ionization threshold, and these states can pass spontaneously into the ionized state. Excitation of these states gives absorption lines which are commonly unsymmetrically broadened on the short wavelength side and the widths indicate half lives ranging down to $10^{-15}$ sec or less. These lines have not been observed in emission and presumably radiation transitions are negligible compared with autoionization [4]. Autoionization in some cases makes contributions to the total photoionization that are large compared with the continuous absorption. In the extreme ultraviolet, line emission sources are commonly used and line sources cannot give quantitative information on line absorption processes, although fortuitously the line spectra often overlap the broad absorption lines.

There are some instances of photoionization produced in a two step process by line absorption below the first ionization potential. Thus Foote and Mohler [7] found that there is some ionization by line absorption in cesium vapor. The efficiency of ionization is proportional to the pressure, and it can be explained by the assumption that highly excited atoms react with neutral atoms to form molecule ions [8]. This and other similar pressure dependent reactions will not be included in this survey.
In the photolionization of molecules the number of ions produced may be less than the number of quanta absorbed and the ratio (here expressed in percent) is called the efficiency of photolionization. Commonly the efficiency is low near the threshold.

In the ionization of molecules the products can be either molecule ions or fragment ions, and it requires a mass spectrometric analysis to obtain a complete interpretation of the results. In practice it is best to measure the ionization cross section in a simple ionization chamber and use the mass spectrometric measurement to evaluate relative abundances of different ions.

.2. EXPERIMENTAL METHODS

The rare gases are purely monatomic and a direct measurement of the continuous absorption affords the simplest method of evaluating the atomic cross section for photolionization. There is the complication that the continuous spectra fall in the extreme ultraviolet and nearly all window materials are opaque to this radiation. Effective sources for the far ultraviolet are intense discharges in hydrogen, helium or argon, or high vacuum sparks between metal electrodes. In any case, it is essential to separate the discharge region and the gas being studied. Weissler and his colleagues [1] have used a differential pumping chamber between the source and the spectrometer entrance slit. Ditchburn [36] has found it feasible to use thin sheets of collodion over the slit to separate the discharge and the gas being studied.

High temperatures and chemical reaction with windows are a difficulty in measurements with most of the metal vapors. Ditchburn and his associates [16] have used a tube of the following design to keep windows cool and clear. The metal vapor is confined by two metal plugs to the central half of a nickel tube about 2 meters long. These plugs are about 10 cm long with holes 6 mm in diameter along the axis. The mid-section is held at a temperature which gives a convenient vapor pressure, the plugs are at a slightly higher temperature, and the rest of the tube is cool. Helium at roughly 1 cm pressure is in the tube, and this slows up the diffusion of the metal and keeps it from reaching the windows. The experimental uncertainty in the vapor pressure, temperature data is probably the major source of uncertainty.

Intensity measurements can be made either by a photomultiplier or by photographic densitometry. Electrical measurements can give better precision, but photographs give optimum resolving power which is important when autolionization peaks are present. In measurements at wavelengths of less than 1000A, sources giving line emission spectra are commonly used and autolionization cannot be measured quantitatively.
Measurements of photolization cross sections can be made by passing a beam of radiation through a simple parallel plate ionization chamber in gas at a measured pressure. The beam strikes a thermopile or the sensitized surface of a photomultiplier bulb which measures the photon flux [5]. A surface of sodium salicylate gives a nearly constant quantum sensitivity in the range (to about 1000A) in which it is feasible to calibrate it with a thermopile. Weissler's group have used two or three ionization chambers spaced along a tube containing the gas to measure both the absorption and the photolization [6].

In pioneer studies of photolization of cesium vapor, Foote and Mohler [7] used the space charge effect of positive ions on thermionic emission from a hairpin cathode to detect photolization. When the voltage in a diode is reduced to one or two volts the current is limited by space charge and there is a potential minimum in the region around the filament. If positive ions are produced in this region, they are trapped and neutralize the space charge. One ion can liberate more than $10^4$ electrons and this large amplification factor made it simple to measure photolization as a function of wavelength. Absolute measurements were made at a few wavelengths with a simple ionization chamber and measured radiation flux [19].

Mass spectrometric research on photolization of molecules is with one notable exception a relatively new field of research. In 1932 Terenin and Popov [9] found that thallium iodide, bromide and chloride are ionized by radiation transmitted by a quartz monochromator. A simple magnetic spectrometer showed that the ions are Tl$^+$ and I$^-$ or Br$^-$ for the iodide or bromide. The ion current reached a peak value near 2125A for Tl I and 2000A for Tl Br. The cross section for photolization was of the order of $10^{-17}$ cm$^2$.

In recent years Hurzeler, Inghram, and Morrison [10] have used a mass spectrometer to study ionization products produced by resolved ultraviolet radiation transmitted by a lithium fluoride window. They reported on a variety of organic molecules which are ionized by radiation of wavelength greater than 1080A. Weissler, Samson, Ogawa and Cook [46] measured mass spectra of photoionization products without a window between the monochromator and the ionization chamber, and preliminary results have been published for O$_2$, N$_2$, CO, NO, CO$_2$, N$_2$O and NO$_2$. 

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Lassettre and his staff at Ohio State University have made careful measurements of the probability of inelastic scattering of 500 ev electrons as a function of the energy lost in collision. Studies include helium, nitrogen, oxygen, carbon monoxide, carbon dioxide and water [13]. He assumes with supporting evidence that at 500 ev the Born approximation is valid and probabilities of inelastic collision can be related to probabilities of photon absorption. This affords an alternative method of deriving photoionization cross sections that avoids the difficulties of far ultraviolet research. Results seem to be consistent with optical measurements, but resolving power is less and except in helium transitions to discrete states tend to mask the continua.

3. EXPERIMENTAL RESULTS

3.1. Foreword

The following summary of experimental results gives photoionization cross sections for atoms and some molecules. The section on molecules is limited to common diatomic molecules and simple polyatomic molecules, with particular attention to molecules that might be found in the upper air. With a few exceptions, the list is limited to researches affording a quantitative basis for estimating atomic or molecular cross sections for photoionization.

For each atom, following the chemical symbol for the element, the ionization threshold is given in angstrom units and in electron volts. The configuration is given for the normal state or for the ionized states in customary spectral notation. Data are taken from Charlotte Moore's "Circular on Atomic Energy Levels" [11]. The elements are arranged according to columns of the periodic table beginning with hydrogen and the alkalies.

For molecules spectral notation of the normal state is not given. The threshold is commonly the first of a group of "Rydberg series limits" and some information on the other limits is given.

Figures showing atomic or molecular cross sections as a function of wavelength or electron volts are given for nearly all the atoms and molecules. These are all taken from the sources indicated without editing and a variety of coordinates are used. In this field a common unit of cross section is the "megabarn", Mb, which is $10^{-18}$ cm$^2$. 

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3.2. Photoionization Cross Sections of Atoms

H \hbar = 912A \quad 13.595 \text{ ev} \quad \text{Normal state} \quad 1s^2S_{1/2}

There are no experimental measurements of \( \sigma \), but the theory is reliable and gives as a good approximation [14]

\[
\sigma = 6.33 \times 10^{-18} (\lambda / \lambda_0)^3
\]

Li \hbar = 2300A \quad 5.390 \text{ ev} \quad \text{Normal state} \quad 2s^2S_{1/2}.

Tunstead [15] measured the absorption cross section in the range 2300A to 1800A. \( \sigma_0 (2300A) \) is \( 2.5 \pm 0.5 \times 10^{-18} \text{ cm}^2 \), \( \sigma \) decreases with decreasing wavelength, and \( \sigma (1800A) \) is \( 1.35 \times 10^{-18} \). It decreases in this range as \( \lambda^{2.5} \). See figure 1.

Na \hbar = 2412A \quad 5.138 \text{ ev} \quad \text{Normal state} \quad 3s^2S_{1/2}

Ditchburn, et al., [16] measured the absorption cross section in the range 2412 to 1600A, and Hudson [17] has extended the measurements to 1100A.

\( \sigma_0 (2412A) = 0.116 \pm 0.012 \times 10^{-18} \text{ cm}^2 \) and drops sharply to \( 0.013 \times 10^{-18} \) at 1950A and rises to a sharp maximum \( \sigma = 0.4 \times 10^{-18} \) at 1400A, and is less than \( 0.01 \times 10^{-18} \) at 1100A. See figure 2. A correction for molecular absorption has been made [16] by measuring absorption as a function of pressure and extrapolating to low pressure.

K \hbar = 2856A \quad 4.339 \text{ ev} \quad \text{Normal state} \quad 4s^2S_{1/2}

Ditchburn, Tunstead and Yates [18] measured the absorption coefficient to 1600A and measurements at different pressures gave a correction for some molecular absorption.

\( \sigma_0 (2856A) = 0.012 \pm 0.003 \times 10^{-18} \text{ cm}^2 \) and drops to \( 0.008 \times 10^{-18} \) at 2700A, and rises to \( 0.24 \times 10^{-18} \) at 1600A. See figure 3.

Photoionization measurements confirm the shape of the absorption curve to 2200A [19, 20].

K \(_2\) amounts to less than 3 percent of the vapor at the highest vapor pressures and the absorption is negligible to 2100A but \( \sigma (K_2) \) rises to roughly \( 10 \times 10^{-18} \) at 1700A [22].

Rb \hbar = 2968A \quad 4.176 \text{ ev} \quad \text{Normal state} \quad 5s^2S_{1/2}

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Mohler and Boeckner [19] measured photoionization in the range 2968A to 2300A. They used the space charge effect combined with a measurement in a simple ionization chamber with radiation of measured quantum flux.

\[ \sigma_0 (2968A) = 0.11 \times 10^{-18} \text{ cm}^2. \] \( \sigma \) drops rapidly with decreasing \( \lambda \) reaching nearly 0 at 2550A and remains low to 2300A. See figure 4.

Beutler [21] has observed 39 absorption lines in the range 810A to 594A which presumably give autoionization. They fall in series that converge to \(^3\)P and \(^1\)P limits of the configuration \(4p^5\) 5s.

Cs \[ \lambda_0 = 3184A \quad 3.893 \text{ ev} \quad \text{Normal state} \quad 6s^2 \frac{2}{3}S_{1/2} \]

Braddock and Ditchburn [22] measured the absorption from 3184A to 2300A.

\[ \sigma_0 (3184A) = 0.22 \pm 0.01 \times 10^{-18} \text{ cm}^2 \] and drops to \(0.078 \times 10^{-18}\) near 2800A and rises to \(0.15 \times 10^{-18}\) near 2400A. See figure 5. The absorption is proportional to the pressure. Mohler and Boeckner [19] measured the photoionization in this range. Their values are \(\sigma_0 = 0.23 \pm 0.02 \times 10^{-18}\) \(\sigma\) reaches a minimum of \(0.043 \times 10^{-18}\) near 2600A and rises to \(0.08 \times 10^{-18}\) near 2200A. Beutler and Guggenheimer [23] find absorption lines beginning at 999A which converge to \(^3\)P and \(^1\)P limits 721A, 719A, 651A and 649A of the configuration \(5p^5\) 6s.

Mg \[ \lambda_0 = 1610A \quad 7.64 \text{ ev} \quad \text{Ionized state} \quad 3s^2 \frac{2}{3}S \]

Ditchburn and Marr [24] have measured absorption from 1610A to 1450A. \(\sigma_0 (1610A) = 1.18 \pm 0.25 \times 10^{-18}\) cm\(^2\) and \(\sigma\) decreases sharply to \(0.2 \times 10^{-18}\) at 1450A. The absorption is directly proportional to the pressure. See figure 6.

Ca \[ \lambda_0 = 2028A \quad 6.11 \text{ ev} \quad \text{Ionized state} \quad 4s^2 \frac{2}{3}S \]

\[ \lambda_0 = 1589A \quad 7.82 \text{ ev} \quad \text{Ionized state} \quad 3d^2 \frac{5}{2}D_{3/2} \frac{3}{2} \]

Jutsum [26] and Ditchburn and Hudson [25] have measured absorption in the range 2028A to 1100A. This is characterized by continuous absorption beyond 2028A and 1589A and by two series of absorption lines, much broadened by autoionization in the range 1900A to 1589A. The absorption series involve double excitation of the two valence electrons into a 3d level and into p levels. For the continuum \(\sigma_0 (2028A) = 0.45 \pm 0.07 \times 10^{-18}\) cm\(^2\) and this drops sharply to zero near 1950. In the range 1900A to 1589A it rises to about \(0.45 \times 10^{-18}\) but this range is partly masked by line absorption. At 1589A it rises to \(0.9 \times 10^{-18}\) and falls to a flat minimum of \(0.32 \times 10^{-18}\) near 1250A and is \(0.55 \times 10^{-18}\) at 1100A.
The first autoionization lines of the singlet P series have peak absorption coefficients of $30 \times 10^{-18}$ and $70 \times 10^{-18}$ and half-widths of $615 \text{ cm}^{-1}$ and $69 \text{ cm}^{-1}$. See figures 7 and 8.

\[ \lambda_o = 2143A \quad 5.785 \text{ ev} \quad \text{Normal state} \quad 5s^2 \, 5p \, ^2p_{1/2} \]

Garton [29] has published a qualitative description of the absorption from 2143A to 1400A. Absorption decreases from 2143A to nearly zero at 1800A and five intense diffuse absorption lines at 1757.3A, 1740.9A, 1711.1A, 1676.2A and 1648.7A dominate in intensity. These lines come from the configuration $5s \, 5p^2$. Marr [30] has measured the maximum atomic absorption coefficient of the 1757A line as about $10^{-16} \text{ cm}^2$ and estimates the continuous absorption coefficient $\sigma_0$ (2143A) to be one percent or less of this or of the order of $10^{-18}$.

\[ \lambda_o = 2030A \quad 6.106 \text{ ev} \quad \text{Normal state} \quad 6s^2 \, 6p \, ^2p_{1/2} \]

Marr [27] has measured the absorption in the range 2030A to 1450A. Very intense wide autoionization lines tend to mask the continuum [28].

$\sigma_0$ (2030A) = $4.5 \times 10^{-18} \text{ cm}^2$. $\sigma$ drops to $2.1 \times 10^{-18}$ at 2010A. At 1950A it is $4.8 \times 10^{-18}$ and drops to $0.7 \times 10^{-18}$ at 1750A. Three autoionization peaks are

<table>
<thead>
<tr>
<th>$\lambda$</th>
<th>$\sigma$ max.</th>
<th>$f$ number</th>
<th>half width</th>
<th>half life</th>
<th>Term</th>
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<tr>
<td>2007</td>
<td>$12 \times 10^{-18}$</td>
<td>.005</td>
<td>300 cm$^{-1}$</td>
<td>$18 \pm 5 \times 10^{-15} \text{ sec}$</td>
<td>$^4p_{3/2}$</td>
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<tr>
<td>1610</td>
<td>$150 \times 10^{-18}$</td>
<td>.52 ± .09</td>
<td>2450 cm$^{-1}$</td>
<td>$2.2 \times 10^{-15} \text{ sec}$</td>
<td>$^2D$</td>
</tr>
<tr>
<td>1490</td>
<td>$30 \times 10^{-18}$</td>
<td>.005</td>
<td></td>
<td></td>
<td>$^2p$</td>
</tr>
</tbody>
</table>

These come from the configuration $6s \, 6p^2$. The "$f$ number" for the continuum is 0.025. See figure 9.

He

\[ \lambda_o = 504.3A \quad 24.58 \text{ ev} \quad \text{Ionized state} \quad 1s \, ^2S \]

Lee and Weissler [31] measured the absorption in the range 504A to 240A. Axelrod and Givens [32] extended the measurements to 150A. Dershem and Schein [33] in 1931 measured the absorption coefficient of K $\alpha$ of carbon ($\lambda = 44.6A$) in He.

Lee and Weissler [31] find $\sigma_0$ at 504A = $7.1 \pm .7 \times 10^{-18} \text{ cm}^2$. $\sigma$ (400A) = $4.0 \times 10^{-18}$, $\sigma$ (300A) = $1.66 \times 10^{-18}$, $\sigma$ (240A) = $.92 \times 10^{-18}$. Axelrod and Givens [32] find somewhat larger values at the shorter wavelengths. $\sigma$ (300A) = $2.3 \times 10^{-18}$, $\sigma$ (250A) = $1.6 \times 10^{-18}$, $\sigma$ (200A) = $.95 \times 10^{-18}$, $\sigma$ (170A) = $.73 \times 10^{-18} \text{ cm}^2$. See figure 10. Dershem and Schein [33] find $\sigma$ (44.6A) = $.0238 \times 10^{-18} \text{ cm}^2$. 

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Between 504A and 200A, $\sigma$ decreases as $\lambda^{2.18}$. Between 200A and 44.6A, $\sigma$ decreases as $\lambda^{2.46}$.

Wheeler [34] has computed the theoretical value as $\sigma_o = 7.4 \times 10^{-18}$.

Lee and Weissler [35] and Ditchburn [36] have measured the absorption to 240A and 200A respectively. Data are consistent within the range of experimental uncertainty. Ditchburn gives $\sigma_o (577A) = 4 \times 10^{-18}$ cm$^2$ and $\sigma$ rises to a flat maximum of $8 \times 10^{-18}$ near 400A and falls to $5 \times 10^{-18}$ near 256A and jumps to $7.5 \times 10^{-18}$ at 256A and falls to $5 \times 10^{-18}$ near 200A. See figure 11.

Dershem and Schein [33] find for the absorption coefficient of carbon K $\alpha$ (44.6A) $\sigma = 0.436 \times 10^{-18}$ cm$^2$. From 256A to 44.6A $\sigma$ decreases as $\lambda^{1.6}$.

The continuous absorption measurements give $\sigma_o (778A) = 36 \times 10^{-18}$ cm$^2$. This is nearly constant to 700A and drops smoothly to $14 \times 10^{-18}$ near 424A. It jumps to $19 \times 10^{-18}$ at 424A and falls smoothly to $8 \times 10^{-18}$ at 360A. See figure 12.

Wainfan, Walker and Weissler [38] measured photolonization in the range 787A to 500A with values consistent with the absorption measurements.
Anne Pery-Thorne and Garton [39] have measured absorption in the range 885Å to 500Å. The continuum was measured by photomultiplier and the line absorption by photographic densitometry.

Between 885Å and 845Å the continuum is partially masked by broad lines [40] converging at $^{2p}_{1/2}$.

$\sigma_o$ (885Å) is about $30 \times 10^{-18}$ cm$^2$ and $\sigma_o$ (845Å) is $37 \pm 7 \times 10^{-18}$. $\sigma$ remains nearly constant to 600Å and drops to $30 \times 10^{-18}$ at 500Å. See figure 13. They measured the integral of the absorption across each line for doublets between 881Å and 851Å. The $f$ numbers for the first two doublets are: 881Å, $f = 0.0131$; 869.5Å, $f = 0.0235$; 862.7Å, $f = 0.0143$; 858.5Å, $f = 0.0086$.

3.3. Photolonization Cross Section of Some Molecules

$H_2$

$\lambda_o = 804.13$Å [43] 15.42 ev

Lee and Weissler [41] measured the continuous absorption in the range 800Å to 300Å, and found autoionization bands superposed on the continuum in the range 770Å to 670Å. Beulter and Junger [43] have described the band system giving rise to autoionization. The rotational fine structure of this band system suddenly become diffuse beyond 804.13Å.

The continuum rises abruptly from 804Å to a value of $\sigma = 7.4 \times 10^{-18}$ cm$^2$ near 750Å, and drops gradually to $4 \times 10^{-18}$ at 400Å and less than $7 \times 10^{-18}$ at 300Å. See figure 14.

Wainfan, Walker and Weissler [38] measured photolonization cross section and photolonization efficiency from 800Å to 650Å. The efficiency is nearly 100 percent and the maximum value of $\sigma_1 = 8.3 \times 10^{-18}$ cm$^2$. Values for the bands are not quantitative, as a line source was used.

Schönheit [42] has published a note on the mass spectrum of the photolonization products. At 637Å (19.5 ev) the relative abundance of ions was: $H_2^+$ is 1.00; $H^+$ is 0.10; $H_3^+$ (from collisions of $H_2^+$ and $H_2$) is 0.03. The appearance potential of $H^+$ is 18.05 ev [48].

$N_2$

$\lambda_o = 795.74$Å 15.503 ev [47]

$\lambda_o$ belongs to a group of Rydberg series limits at 796Å, 742Å, 661Å and 526Å. Band systems converging at levels beyond 796Å, give autoionization peaks superposed on the continuum [47]. Measurements of autoionization are not quantitative.

Weissler, Po Lee and Mohr [44] measured absorption in the range 796Å to 300Å, and Curtis [45] measured absorption to 150Å.
Wainfan, Walker and Weissler [38] measured photolonization in the range 796Å to 500Å and found nearly 100 percent efficiency beyond 750Å.

Weissler, Samson, Ogawa and Cook [46] measured the mass spectrum of the ions produced by photolonization for wavelengths down to 400Å.

Weissler, et al., [44] find the continuum rises abruptly from the threshold to \( \sigma = 25 \times 10^{-18} \) near 750Å. \( \sigma \) is about \( 22 \times 10^{-18} \) at 670Å and \( 27 \times 10^{-18} \) near 660Å and falls almost linearly to about \( 7 \times 10^{-18} \) at 300Å. See figure 15. Curtis [45] finds a similar curve but gives absolute values about half the values reported by others. Mass spectra show that N⁺ appears at 510Å (24.3 ev) and from 480Å to 400Å the abundance is nearly constant and about one percent of N₂⁺. The threshold for N⁺ is consistent with appearance potential measurements [48].

\[
O_2 \quad \lambda_0 = 1026.5Å \quad 12.09 \text{ ev}
\]

Rydberg series converge to limits 1026.5Å, 770Å, 729Å, 681Å and 611Å [47]. Autolonization peaks occur in this range.

Weissler and Po Lee [49] and Po Lee [50] have measured absorption in the range 1300Å to 200Å.

Watanabe and Marmo [51] measured photolonization and absorption in the range 1026Å to 850Å using a continuous emission source.

Wainfan, Walker and Weissler [38] measured photolonization cross sections to 473Å, and Weissler, Samson, Ogawa and Cook [46] measured the mass spectrum.

Po Lee [50] used relatively high resolution. In the range 1026Å to 675Å autolonization peaks partially mask the true continuum. The continuum rises from the threshold to a value of \( \sigma = 2.0 \times 10^{-18} \) cm² at 970Å, \( 4.0 \times 10^{-18} \) at 920Å, and \( 3.0 \times 10^{-18} \) at 850Å. From 850Å to 740Å it is masked by autolonization bands, but rises to about \( 20 \times 10^{-18} \) at 740Å and remains about this value to 500Å and drops to \( 12 \times 10^{-18} \) near 200Å. See figure 16.

Watanabe and Marmo [51] measured the efficiency of ionization from 1026Å to 850Å. It ranges from 50 percent to 100 percent, and the more intense autolonization bands are about 5 times as strong as the background continuum. Values of \( \sigma \) for the continuum are consistent with Po Lee's values. Photolonization measurements in the far ultraviolet [38] give a nearly constant value of \( \sigma_i = 25 \times 10^{-18} \) cm² in the range 700Å to 473Å. This is in fair agreement with Po Lee's absorption measurements (\( \sigma = 20 \times 10^{-18} \)).
The mass spectrum [46] shows that \(0^+\) appears at 662A (18.8 ev) and rises to a peak near 630A. A second nearly equal peak begins at 603A (20.7 ev). There is some evidence of a third increase near 530A (23.4 ev). The three critical potentials could give the products \(0^+\left(^4S\right) + 0\) (\(3P\)), \(0^+\left(^4S\right) + 0\) (\(^1D\)) and \(0^+\left(^4S\right) + 0\) (\(^1S\)) at 18.7 ev, 20.7 ev and 22.9 ev. \(0^+\) currents are roughly 10 percent of the \(0_2^+\) currents and make a relatively small contribution to the total absorption. The \(0_2^+\) curve gives a series of six sharp peaks, probably from autoionization, that conceal the continuum found by Po Lee using higher resolving power.

\[\lambda_0 = 884.7A \quad 13.94 \text{ ev} \ [53]\]

Three Rydberg series limits are at 884.7A, 749.7A, and 630.2A [52, 53].

Sun and Weissler [55] measured the absorption in the range 885A to 374A.

Watanabe [54] measured the photoionization near the threshold.

Weissler, Samson, Ogawa and Cook [46] measured photoionization with a mass spectrometer to 400A.

Photoionization begins with a steep increase at the threshold 884.7A. The continuum, partially masked by autoionization peaks, has a broad flat maximum near 500A of \(\sigma = 18 \times 10^{-18} \text{ cm}^2\). It is \(15 \times 10^{-18}\) or more from 700A to 400A, and \(13 \times 10^{-18} \text{ cm}^2\) at 374A. See figure 17.

\(C^+\) appears near 596A (20.8 ev). It remains less than one percent of \(CO^+\) to 556A (22.3 ev) and then increases to two percent of \(CO^+\). There is some evidence of increases at 24.8 ev and 26.4 ev. These critical potentials have also been observed in electron impact studies [48] and are ascribed to transitions to \(C^+\left(^2P\right) + 0^-\left(^2P\right)\), \(C^+\left(^2P\right) + 0\) (\(3P\)), \(C^+\left(^2P\right) + 0\) (\(^1D\)) and \(C^+\left(^2P\right) + 0\) (\(^1S\)). \(0^+\) was not observed in photoionization, but is produced by electron impact ionization at 24.7 ev [48].

\[\lambda_0 = 900A \quad 13.79 \text{ ev} \ [56]\]

There is a second Rydberg series limit at 690A, 18.07 ev [56].

Sun and Weissler [55] measured the absorption coefficient in the range 900A to 374A. Nicole Damany-Astoin, et al., [57] measured absorption to 167A.

Wainfan, Walker, and Weissler [38] measured photoionization cross sections and efficiencies to 473A.
Weissler, Samson, Ogawa and Cook [46] measured photoionization in a mass spectrometer to 450A.

The photoionization continuum rises sharply from the threshold to \( \sigma = 19 \times 10^{-18} \text{ cm}^2 \) near 800A and near 690A rises again reaching a flat maximum near 600A of \( 32 \times 10^{-18} \text{ cm}^2 \) (Sun and Weissler [55]) or 29 \times 10^{-18} \text{ cm}^2 \) (Damanay-Astoin [57]). See figure 18. Damanay-Astoin finds a minimum at 415A (29.6 ev) with \( \sigma = 16 \times 10^{-18} \text{ cm}^2 \) [57], and \( \sigma \) rises sharply to a broad maximum of 24 \times 10^{-18} \text{ cm}^2 \) near 370A. There is a second sharp minimum of \( \sigma = 9 \times 10^{-18} \text{ cm}^2 \) at 294A (42 ev) and a sharp rise to a third maximum of \( \sigma = 23 \times 10^{-18} \) near 270A. From this point \( \sigma \) decreases smoothly to zero at 167A.

Wainfan, et al., find a photoionization efficiency ranging from 60 to 100 percent from 900A to 473A. There are many autoionization peaks in the range covered.

Mass spectra show \( 0^+ \) increasing to a peak at 646A (19.2 ev) at 610A (20.3 ev) and at 556A (22.3 ev). The cross section at 630A for \( \sigma (0^+) \) is about \( 1.4 \times 10^{-18} \). \( CO^+ \) appears near 636A (19.5 ev) and increases at 605A (20.5 ev). The cross section at 630A is \( \sigma \) (\( CO^+ \)) = \( 0.3 \times 10^{-18} \text{ cm}^2 \). Appearance potentials of \( 0^+ \) at 19.2 ev and at 22.3 ev are correlated with processes, \( CO + 0^+ (4S) \) and \( 0^+ (2D) \). The two appearance potentials of \( CO^+ \) could be ascribed to \( CO^+ + 0^- (2P) \) and \( CO^+ + 0 (3P) \) but there is some excess kinetic energy [46].

\[ \lambda_0 = 1340A \quad 9.25 \text{ ev} \quad [58] \]

There are also Rydberg series limits [58] at 871.5A (14.15 ev), 748.5A (16.48 ev), 678.4A (18.19 ev) and 676.8A (18.23 ev).

Sun and Weissler [60] measured absorption in the range 1800A to 374A, and Granier and Astoin [63] extended the range to 150A.

Watanabe [59] measured photoionization with a continuous source, and good resolution showing separate vibration states of NO and NO\(^+\). See figure 19. Walker and Weissler [61] measured photoionization efficiency to 640A.


The photoionization continuum increases almost linearly except for vibration fine structure from 1340A to a value of \( 18 \times 10^{-18} \text{ cm}^2 \) near 900A, drops to about \( 8 \times 10^{-18} \) near 780A, rises to a flat maximum of \( 20 \times 10^{-18} \) near 600A, drops to \( 13 \times 10^{-18} \) at 308A, rises to a maximum of \( 20 \times 10^{-18} \) near 260A and falls to \( 12 \times 10^{-18} \) near 200A. There are autoionization peaks in most of this spectrum. Figure 20 gives the spectrum to 300A.
0\(^+\) appears near 636A (19.5 ev), reaches a flat maximum near 620A and rises again at 600A (20.7 ev) to a second flat maximum. The 0\(^+\) current is at the maximum about 2 percent of the NO\(^+\) current in this range. N\(^+\) appears at 570A (21.8 ev) and rises to a maximum near 540A of about 5 percent of the NO\(^+\) current. 0\(^+\) probably comes from the dissociation into 0\(^+\) (4S) + N (4S) and N (2D) at 19.5 ev and 20.7 ev respectively. N\(^+\) comes from N\(^+\) (3P) + O (3P) [46].

\[
\begin{align*}
\text{N}_2\text{O} & : \lambda_0 = 961\text{A} & 12.94 \text{ ev} \ [62] \\
\text{NO}_2 & : \lambda_0 = 1270\text{A} & 9.78 \text{ ev} \ [65]
\end{align*}
\]

Other Rydberg series limits give energy levels of 16.39 ev, 16.55 ev and 20.10 ev [62].

Astoin and Grainier [64] measured the absorption to 160A.

Walker and Weissler [61] measured the photoionization efficiency and cross section in the range 960A to 687A. Weissler, Samson, Ogawa and Cook [46] measured the mass spectrum of the photoionization products.

The photoionization continuum rises sharply from the threshold to a flat maximum near 700A of 32 x 10\(^{-18}\) cm\(^2\) [64], or 30 x 10\(^{-18}\) cm\(^2\) [61]. There is a minimum of 17 x 10\(^{-18}\) cm\(^2\) near 500A, a second flat maximum near 360A of 30 x 10\(^{-18}\) cm\(^2\), a well defined minimum at 263A of about 13 x 10\(^{-18}\) cm\(^2\), a third maximum of the same size near 300A and the absorption drops to 4 x 10\(^{-18}\) at 160A. There are many autoionization peaks in the entire range. See figure 21. NO\(^+\) begins near 810A (15.3 ev) and rises rather irregularly to a value at 650A of 1.3 times the N\(_2\)O\(^+\) current and remains about 30 percent greater than N\(_2\)O\(^+\) to 500A. N\(^+\) appears near 710A (17.4 ev) and rises abruptly to a value about 16 percent of N\(_2\)O\(^+\) and remains of this magnitude to 500A. N\(^+\) appears at 620A (20.0 ev) and is roughly 10 percent of N\(_2\)O\(^+\). 0\(^+\) appears near 810A, 15.3 ev and is roughly 10 percent of N\(_2\)O\(^+\). See figure 22.

Nakayama, Kitamura and Watanabe [65] measured the photoionization from the threshold to 1080A. Weissler, Samson, Ogawa and Cook [46] measured the mass spectrum in the range 1100A to 500A.

Nakayama, et al., find the ionization efficiency very low (.03 to 2 percent) at \(\lambda\) greater than 1200A. There is an increase in the ionization continuum at 1145A (10.83 ev). Near 1100A \(\sigma_1\) is about 2.2 x 10\(^{-18}\) cm\(^2\).

Weissler, et al., find both NO\(_2\)\(^+\) and NO\(^+\) appearing near 1100A (11.3 ev). Beyond 950A, NO\(^+\) becomes greater than NO\(_2\)\(^+\) and at 645A is 3.5 x NO\(_2\)\(^+\). Both NO\(_2\)\(^+\) and NO\(^+\) curves show 5 or 6 sharp peaks in the range 1100A to 500A. Four of these seem to be common to both curves. They may well be autoionization peaks, but this is an opinion of the reviewer.

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$O^+$ appears at 17.6 ev (700A) and rises to a value of about .75 x NO$_2^+$ at 645A. Weissler, et al., do not give absolute values of $\sigma$ for these ionization processes. There is conflicting evidence as to the first ionization potential in electron impact research [48] as well as in these experiments. Nakayama, et al., suggest that 10.83 ev may be the appearance potential for NO$_2^+ \rightarrow$ NO$^+$ and O$^-$. Weissler, et al., give this as 11.3 ± .4 ev.

$$H_2O \quad \lambda_0 = 986A \quad 12.59 \text{ ev} \quad [66]$$

Watanabe [66] measured the photoionization threshold. Nicole Astoin [67] measured the continuous absorption coefficient in the range 986A to 160A. There is banded absorption superposed on the continuum. Wainfan, Walker and Weissler [38] measured the photoionization efficiency and cross section in the range 986A to 450A. The efficiency is about 40 percent in the range 986A to 900A, and from 950A to 450A is from 70 to 100 percent. $\sigma_i$ rises at a fairly constant rate to 20 x $10^{-18}$ cm$^2$ near 625A [38]. See figure 23. Nicole Astoin finds for $\sigma_a$ a value of 21 x $10^{-18}$ cm$^2$ at 625A. It drops to a sharp minimum of 11 x $10^{-18}$ at 512A and rises to 28 x $10^{-18}$ cm$^2$ at 435A and falls to 2 x $10^{-18}$ cm$^2$ at 167A. The experimental uncertainties are about 20 percent. Mass spectra of the ions have not been studied.

$$CH_4 \quad \lambda_0 = 955A \quad 12.99 \pm .01 \text{ ev} \quad [66]$$

Watanabe [66] has measured the photoionization threshold. Sun and Weissler [68] and Ditchburn [69] have measured the continuous absorption to 400A and 300A respectively. Wainfan, Walker and Weissler [38] have measured the efficiency of photoionization and the photoionization cross section to 500A.

The efficiency of ionization increases from 0 to 100 percent between 955A and 800A. $\sigma_i$ rises sharply to a flat maximum of 39 x $10^{-18}$ cm$^2$, 44 x $10^{-18}$ cm$^2$ or 60 x $10^{-18}$ near 800A using measurements of Sun and Weissler [68], Ditchburn [69] or Wainfan, Walker and Weissler [38] respectively, and the ionization efficiency data of the latter. $\sigma_i$ decreases regularly with decreasing wavelength to 13.1 x $10^{-18}$ cm$^2$ at 374A and 4 x $10^{-18}$ cm$^2$ at 278A according to Ditchburn (Sun and Weissler give a nearly equal value at 374A). See figure 24.

The mass spectrum of photoionization products has not been studied. The $\sigma_i (\lambda)$ curve is simpler than those found for the diatomic and triatomic molecules with no evidence of autoionization states or higher ionization potentials.
4. SUMMARY

It is evident that much more research is needed in the field of photoionization of atoms and simple molecules. Thus, while some work has been done on all the alkali vapors, only in the case of sodium do the measurements extend far enough to permit an estimation of the number of the continuum. There is some data on all the rare gases except xenon and something on four other elements. In the case of molecules, the reviewer has limited this report to a few common gases. There are data on photoionization thresholds for several hundred polyatomic molecules [67] and in some cases there are measurements of \( \sigma \) from the threshold to about 1000A.

Quantitative measurements of autoionization transitions are a matter of research interest but it requires a continuous spectrum emission source to measure the integral of \( \sigma \) across the line, and such measurements have not been extended into the far ultraviolet. In some atomic spectra and in nearly all molecular spectra the autoionization peaks interfere seriously with measurements of the continuum. Good resolution is necessary to distinguish the continuum from the autoionization peaks and in complicated spectra photographic methods seem to afford the most conclusive data in spite of the inherent limitations of photographic densitometry. However, electrical methods and mass spectrometry are required to interpret the results in the case of molecules.

The magnitudes of the photoionization cross sections and the variation with wavelength show a wide variation. Thus, for atoms, \( \sigma \) near the threshold ranges from \( 0.012 \times 10^{-18} \) for potassium to 36 and 37 \( \times 10^{-18} \) for argon and krypton. The figures illustrate the wide variation in the shape of the curves of \( \sigma \) versus wavelength.
5. REFERENCES

Figure 1. The atomic absorption cross section of lithium [15,17].
Figure 2. The atomic absorption cross section of sodium [17,18].
Figure 3. The atomic absorption cross section of potassium [18].
Figure 4. The atomic photoionization cross section of rubidium [19].
Figure 5. The atomic absorption cross section of cesium [22].
Figure 6. The atomic absorption cross section of magnesium [24].
Figure 7. The atomic absorption cross section of calcium from 2028Å to 1900Å showing autoionization by line absorption superposed on a small continuum [25].
Figure 8. The atomic absorption cross section of calcium from 1600Å to 1080Å [25].
Figure 9. The atomic absorption cross section of thallium. In curve A from 1700A to 1450A the ordinate scale is 10⁻¹⁷ cm². Three peaks from line absorption giving autololization are indicated [27].
Figure 10. The absorption coefficient of helium. \( \sigma = 3.7 \times 10^{-20} \text{ K} \)
Solid line theoretical curve, dashed curve and crosses from Axelrod and Givens [32] and dots from Lee and Weissler [31].
Figure 11. The atomic absorption cross section of neon from Pitchburn [36].
Figure 13. The absorption coefficient for continuous absorption in krypton from Perry-Thorne and Garton [39].
Figure 14. The molecular cross section for absorption and ionization in hydrogen [41,38,1].
Figure 15. The molecular cross section for absorption and ionization in nitrogen [44,38,1].
Figure 16. The molecular cross section for absorption and ionization in oxygen [50, 38, 1].
Figure 17. The molecular absorption cross section of carbon monoxide. Dotted curve is continuum [55]. Short lines in upper left show band systems.
Figure 18. Molecular absorption cross section of carbon dioxide. Dotted curve is ionization continuum [55]. Above shows two band systems.
Figure 19. Molecular cross sections for absorption (solid curve) and ionization (dots) in nitric oxide [59]. Arrows show vibration structure.
Figure 20. Molecular cross sections for absorption and ionization of NO in far ultraviolet [1].
Figure 21. Molecular absorption coefficient of nitrous oxide as a function of wave number. Dashed curve is continuous absorption. (Astoin and Granier [64].)
Figure 22. Ions produced by photoionization of nitrous oxide in a mass spectrometer [46].
Figure 23. Molecular cross sections for absorption and photoionization of water vapor [1].
Figure 24. Molecular cross section for absorption and photoionization of methane. (Ditchburn [69] using data of Wainfan, et al., [38] on photoionization efficiency.)
THE NATIONAL BUREAU OF STANDARDS

The scope of activities of the National Bureau of Standards at its major laboratories in Washington, D.C., and Boulder, Colorado, is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section carries out specialized research, development, and engineering in the field indicated by its title. A brief description of the activities, and of the resultant publications, appears on the inside of the front cover.

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