

Absolute photoionization cross sections of atomic oxygen

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The absolute values of the photoionization cross sections of atomic oxygen have been measured from the ionization threshold to 120 Å. An autoionizing resonance belonging to the $2s2p^4(^4P)3p(^3D^o, ^3S^o, ^3P^o)$ transition has been observed at 479.43 Å; and another line, at 389.97 Å. However, although the experimental data are in excellent overall agreement with rigorous close-coupling calculations, which include electron correlations in both the initial final states, there are discrepancies near threshold that may be significant.

INTRODUCTION

In recent years progress has been made in the theoretical understanding of photoionization of closed-shell atoms. In general, electron correlation effects have been found to be very important. Efforts are now underway to extend this understanding to open-shell atoms.¹ However, there is a serious lack of experimental data dealing with open-shell atoms to provide adequate data for comparison to theory. This is understandable because of the problem of producing these atoms. In the present work we have chosen to study atomic oxygen because it can be produced in reasonable numbers in a simple microwave discharge and because of its importance to upper atmosphere research.

The first measurement of the absolute photoionization cross section of atomic oxygen was made by Cairns and Samson² in 1964. Two subsequent measurements were made by Comes *et al.*³ and by Kohl *et al.*⁴ These measurements were made at a few discrete wavelengths from threshold to about 450 Å. However, there is quite a variation between the different measurements, reaching a factor of 2 near threshold.

Huffman *et al.*⁵ and Dehmer *et al.*⁶ have studied the autoionizing structure of atomic oxygen from threshold to 650 Å but do not present absolute cross sections. The photoelectron spectra of atomic oxygen has been studied by Samson and Petrosky showing the presence of excited molecular oxygen in the products of a microwave discharge in O₂.⁷

On the theoretical side, numerous calculations have been made since the earliest calculations by Bates and Seaton in 1949.⁸⁻¹⁹ Again, a large variation in absolute cross sections exists, ranging from a factor of 50% in the 500–600 Å region to a factor of 2 near threshold.

The main aim of the present work was to measure the relative cross sections of atomic oxygen as accurately as possible and over a large wavelength range (120–900 Å). Then to make an absolute measurement at one or two wavelengths allowing the relative values to be placed on an absolute basis. The 584-Å He I and 304-Å He II lines were chosen for the absolute measurement.

EXPERIMENTAL

Atomic oxygen was produced in a microwave discharge by flowing a mixture (in the ratio 1:4) of O₂ and He at ~0.2 Torr through a pyrex tube coated internally with boric acid. The discharged products were constrained to flow past a small orifice leading to the ion chamber of a mass spectrometer (see Fig. 1). A 60-l/s rotary pump maintained a fast flow of the mixture to minimize wall recombination of the oxygen atoms.

The literature describes many materials used for coating flow tubes.²⁰⁻²² These include phosphoric acid, Teflon, hydrofluoric, boric acid, etc. However, we obtained best results with the boric acid treatment. The flow tube was first cleaned with a detergent and rinsed. When dry, a boiling saturated solution of boric acid was poured into the flow tube, coating all of the interior surface, then poured out. The tube was subsequently heated at 200 °C in an oven for about 4–6 h.

The products of a microwave discharge in O₂ are ground-state O(³P) atoms and excited-state O₂(¹Δ) molecules in addition to the residual ground-state molecules. The gas pressure used and the geometry of the flow tube insure sufficient collisions to deexcite most species and thermalize the products. In an identical arrangement used to study the photoelectron spectra of O₂ and O at 584 Å we found the integrated signal from O₂(¹Δ) to be ~1% of O₂(³Σ).⁷ Other authors quote values of 3–10%.²³⁻²⁵ We make use of this information in the derivation, in the Appendix, of $\sigma(O)$ the photoionization cross section of atomic oxygen.

A photoionization-magnetic mass spectrometer with a mass resolution of about 1 in 65 was used to identify the ions produced in the ion chamber. Details of this instrument have been described previously.^{26,27} It was estimated that about 20–30% of O₂ was dissociated as indicated by the decrease in the intensity of O₂⁺ signal from the mass spectrometer when the microwave generator was switched on.

The light source was a spark discharge lamp that produced a rich spectrum of intense lines extending down to about 100 Å.²⁸ The radiation was dispersed by a 2.2 m grazing incidence monochromator.

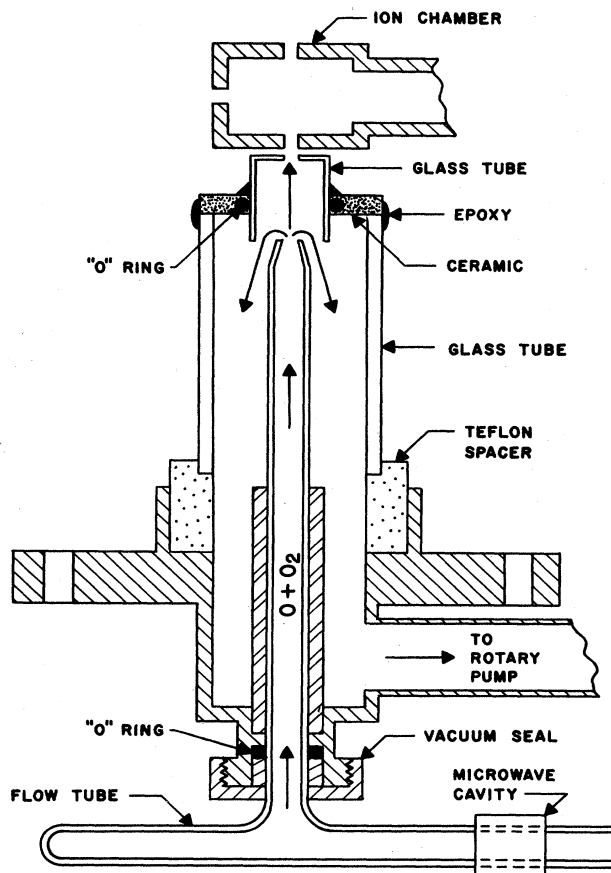


FIG. 1. Diagram of pyrex flow tube and microwave cavity for the production of atomic oxygen.

Our method for measuring the photoionization cross section of atomic oxygen was similar to that used by Comes *et al.*³ but differs in some important details. The measurement procedure was as follows:

The incident radiation was free to pass through the ion chamber of the mass spectrometer and subsequently monitored by a windowless photodiode. The ions produced were mass analyzed and detected with a Johnston type electron multiplier. To eliminate any effects caused by light source intensity variations each ion current was measured simultaneously with the photodiode current. Because O^+ ions were also produced from dissociative photoionization of O_2 it was necessary to measure the ion currents O^+ and O_2^+ with the microwave discharge *off* and *on*. An analysis of the ionization process leads to the following equation for the absolute photoionization cross section of atomic oxygen $\sigma(O)$, see Appendix, Eq. (A14),

$$\sigma(O) = [1/2(1-\alpha)](\Gamma_2 T_2 / \Gamma_1 T_1) [(S'_1 - S_1 \alpha) / S_2] \sigma_{\Sigma} \quad (1)$$

Subscripts 1 and 2 refer to atomic and molecular properties, respectively, and primes indicate measurements made

with the microwave *on*. Thus, Γ_1 and Γ_2 represent the secondary electron emission probability for O^+ and O_2^+ ions, respectively, impinging on the first dynode of the electron multiplier. S'_1 and S_1 represent the O^+ ion signals with the microwave generator *on* and *off*, respectively. S_2 represents the O_2^+ ion signal with no microwave discharge. T_1 and T_2 refer to the transmission of O^+ and O_2^+ ions through the mass spectrometer, respectively. σ_{Σ} is the dissociative photoionization cross section for producing O_2^+ ions from neutral O_2 ground-state molecules (microwave *off*). These cross sections have been tabulated by Samson *et al.*²⁶ The constant α represents the ratio of the O_2 number density with discharge *on* and *off*. That is, $\alpha = n'(O_2) / n_{\Sigma}$, where $n'(O_2) = n'_{\Sigma} + n'_{\Delta}$, which is the sum of the number densities of O_2 molecules in their $^3\Sigma$ and $^1\Delta$ states with the discharge *on*. n_{Σ} is the number density of $O_2(^3\Sigma)$ with discharge *off*. An approximate value for α can be determined by the derivation given in the Appendix, namely,

$$\alpha = S'_2 / S_2 \quad (2)$$

The ratio S'_2 / S_2 was measured at numerous wavelengths within the ionization continuum and was found to be constant within $\pm 1.5\%$. Typical values were 0.7–0.8 depending upon the condition of the boric acid coating. However, when we elected wavelengths that coincided with autoionizing transitions in the O_2 spectrum we found some variation in the ratio. The maximum variation was 10%. From the Appendix we see that the ratio S'_2 / S_2 is weakly dependent on the ratio of the ionization cross sections of $O_2(^1\Delta)$ and $O_2(^3\Sigma)$. If this ratio shows large variations with wavelength, as is likely in autoionizing regions, we can expect the variation observed above.

The relative atomic photoionization cross section can be obtained from Eq. (1) as shown in the Appendix. The term (S_2 / σ_{Σ}) is proportional to the absolute intensity I_0 of the radiation, which in turn is proportional to (i_{ph} / η) , where i_{ph} is the photodiode current and η is the photoelectric efficiency of the cathode. From this we obtain the relation given by Eq. (A18) in the Appendix, namely,

$$\sigma(O) \propto (\eta / i_{ph})(S'_1 - \alpha S_1) \quad (3)$$

Our procedure was to measure the relative cross section over the entire wavelength region by use of Eq. (3). It was important to keep the gas pressure constant during the measurements. This was achieved by use of a Baratron capacitance manometer with a servo-controlled leak valve. After accurate relative cross sections were made they were placed on an absolute basis by determining $\sigma(O)$ from Eq. (1) at 304 Å.

When using Eq. (1) the assumption was made that the transmission factors T_2 and T_1 were equal because both O_2^+ and O^+ ions were formed with thermal energies and were extracted from the mass spectrometer ion chamber with equal energies. To avoid mass discrimination within the ion chamber a repeller plate inside the ion chamber produced a field of approximately 100 V/cm to drive the ions out into the accelerating field of the mass spectrometer where they received an additional 800 V of energy before entering the mass analyzer.

In the development of Eq. (1) in the Appendix the value

of the ratio T_1^D/T_1 is important. This is the ratio of the transmission of energetic atomic oxygen ions produced in the dissociative ionization process to the transmission of thermal energy oxygen ions produced in the microwave discharge. The transmission of ions in any mass spectrometer with narrow entrance and exit slits, as in the present instrument, will be small for ions originally created with excess kinetic energy as in the process of dissociative ionization. This ratio can be determined as follows: By measuring the number of ions/photons transmitted the relative apparent dissociative ionization cross section can be measured. This quantity is normalized to the true dissociative ionization cross section (Ref. 26), σ_{Σ}^D , at threshold where the ion energy is close to zero and the transmission is essentially T_1 . The ratio of this normalized curve to the true value of σ_{Σ}^D yields T_1^D/T_1 . The individual curves are shown in Fig. 2. It can be seen that the ratio varies from 0.2 and 1.0 between 120 and 650 Å.

The steps in the solid line near threshold for the absolute curve represent the vibrational space of the $B^2\Sigma_g^-$ state of O_2 . The heights of the steps are proportional to the transition probabilities. Transitions into this state are followed by predissociation producing the observed O^+ ions.

The value of the relative response of the electron multiplier (Γ_2/Γ_1) to O_2^+ and O^+ ions was measured and found to be 1.08 when the ions impinged with energies ~ 3.9 kV.

RESULTS AND DISCUSSION

The measured absolute photoionization cross sections of atomic oxygen are tabulated in Table I and are shown in Fig. 3 along with the previous experimental results. The results by Cairns and Samson² were influenced by au-

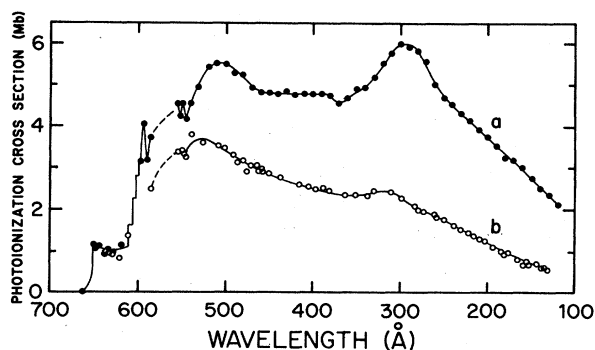


FIG. 2. Dissociative photoionization cross sections for the production of O^+ ions from $O_2(\sigma_{\Sigma}^D)$. Curve *a*: Absolute values. Curve *b*: Relative values influenced by instrumental discrimination against energetic ions. Data normalized at threshold to absolute value where the kinetic energy of the fragment ions is essentially zero. The ratio of the two curves is equal to the transmission T_1^D of the energetic O^+ ions through the mass spectrometer.

TABLE I. Absolute photoionization cross sections of atomic oxygen measured in megabarns ($1 \text{ Mb} = 10^{-18} \text{ cm}^2$).

Wavelength (Å)	Cross sections (Mb)	Wavelength (Å)	Cross sections (Mb)
120.1	1.34	449.01	11.42
130.67	1.95	457.5	12.26
138.4	1.81	462.0	12.22
151.87	2.3	464.3	11.17
154.44	1.93	471.53	11.25
158.92	2.09	479.43	15.6
165.53	2.61	486.6	12.65
176.57	2.63	491.7	12.27
180.25	2.88	501.1	11.76
184.32	3.41	508.5	12.06
192.69	3.58	526.5	12.72
199.60	3.94	537.0	12.11
202.8	3.97	544.7	12.54
215.17	4.47	548.9	12.34
220.95	4.91	551.32	12.57
230.88	5.47	555.5	12.39
250.94	6.09	584.3	13.21
257.8	6.03	585.75	12.93
260.33	6.25	619.1	13.45
279.4	7.10	630.3	13.18
294.5	7.20	634.2	13.41
297.8	7.49	637.3	13.04
304.0	7.70	641.4	12.36
310.0	7.97	644.5	12.71
329.0	8.70	660.9	11.71
337.0	8.46	684.6	8.51
350.88	9.37	700.3	8.28
374.74	9.95	715.65	8.78
389.97	12.07	754.7	4.58
396.6	10.01	767.2	4.30
405.42	11.05	801.1	3.54
409.8	11.02	827.06	3.68
416.0	11.17	834.08	4.28
436.67	11.38		

toionizing structure in atomic oxygen^{5,6} and possibly by structure in the excited $O_2(^1\Delta)$ molecular species. Thus, we have selected from their results only the data points that appear to be free from the effects of structure, and we have shown all their data points in the nonstructured region below 665 Å. The latter data are in very good agreement with our present results. The data of Kohl *et al.*⁴ fall between our earlier results and the present ones and average about 10% higher than the present data. This agreement is significant because of the diverse nature of the three experiments. The results of Comes *et al.*³ are consistently 30 to 50% lower over most of the wavelength range from threshold to 450 Å. Moreover, their equation for obtaining $\sigma(O)$ appears to be missing a factor of 2 in the denominator when compared to our Eq. (1) expressing the same relation. This would further reduce their values relative to the present results.

The experimental data clearly show the contribution to the cross section for producing O^+ ions in their $^4S^o$, $^2D^o$,

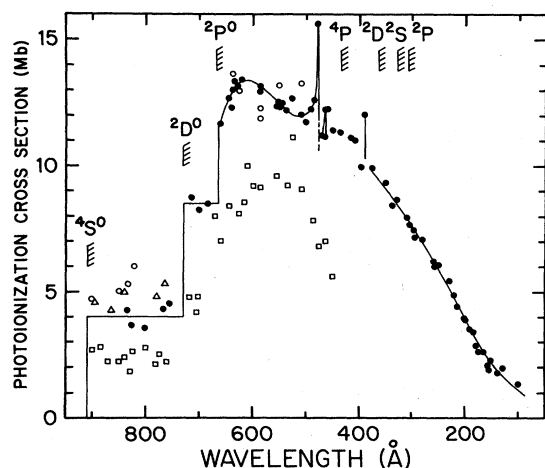


FIG. 3. Absolute photoionization cross sections of atomic oxygen as a function of wavelength. ●, present data; ○, Cairns and Samson (Ref. 2); △, Kohl *et al.* (Ref. 4); □, Comes *et al.* (Ref. 3).

and $2P^o$ states. Care was taken to avoid measurements that coincided with the autoionizing structure preceding the $2D^o$ and $2P^o$ thresholds (tabulated by Huffman *et al.*⁵ and Dehmer *et al.*⁶). However, at wavelengths shorter than the $2P^o$ threshold data were taken at all possible wavelengths because the position of structure is unknown in this region. There is clear evidence of an autoionizing line at approximately 479.4 Å, presumably belonging to a Rydberg series leading to the $4P$ level. Less evident is possible structure at 390 Å. These were chance coincidences with our discrete emission lines. A continuum source of radiation will be used to explore this region in more detail.

The random rms errors of the measured quantities cause a $\pm 7\%$ uncertainty in the relative cross section curve, Eq. (3). The absolute value of $\sigma(O)$ obtained from Eq. (1) has an estimated random rms error of $\pm 9\%$. However, the scatter among the data points is much less than the quoted errors as can be seen from Fig. 3.

We measured the absolute value of $\sigma(O)$ at 584 and 304 Å by use of Eq. (1) and obtained cross sections of 13.6 and 7.7 Mb, respectively. The ratio of these two absolute values is 1.77, whereas the ratios of the relative values obtained by using Eq. (3) gives 1.72. The good agreement of these two ratios is encouraging because they are independent measurements. In Eq. (3) we must use the cross section of Ne to determine η ,²⁹ whereas Eq. (1) requires the dissociative ionization cross sections for producing O_2^+ from O_2 .²⁶

Our present technique should provide accurate relative photoionization cross sections of atomic oxygen. To check that our normalization of the data at 304 and 584 Å to provide absolute cross sections is reasonable we first consider the assumption that the atomic cross section should be approximately equal to one-half the total absorption cross section of molecular oxygen for high energy photons. Figure 4 shows this comparison between $\sigma(O)$ and $\frac{1}{2}\sigma(O_2)$ from 500–120 Å. Over most of the range $\frac{1}{2}\sigma(O_2)$ is within $\pm 10\%$ of the atomic cross section,

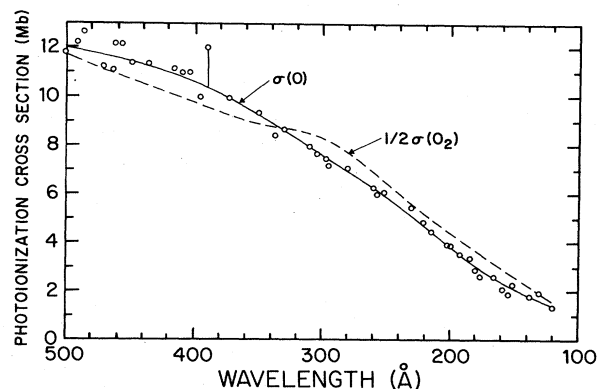


FIG. 4. Comparison of direct photoionization of atomic oxygen, $\sigma(O)$, with one-half the molecular cross section $\frac{1}{2}\sigma(O_2)$, as a function of wavelength.

and there appears to be a convergence between the two curves as they approach 120 Å (103 eV). Of course, there is no reason that the two curves should precisely coincide in this wavelength region. Ejection of valence-shell electrons from the molecules are still important and this can move molecular oscillator strengths from one spectral region to another. In fact, the bump in the $\frac{1}{2}\sigma(O_2)$ curve around 300 Å is caused by an increase in dissociative ionization of O_2 (see Ref. 26), which presumably has stolen oscillator strength from the longer wavelength region. However, we might expect the two curves to agree at higher photon energies, particularly when inner-shell electrons are involved (e.g., K -shell electrons). The work by Henke and co-workers certainly supports this premise.³⁰

A more accurate check on the accuracy of the absolute data is to measure the total oscillator strength for the absorption process. According to the Thomas-Reiche-Kuhn sum rule the total oscillator strength $f(\text{total})$ should equal the number of electrons in an atom or molecule.³¹ Thus,

$$f(\text{total}) = \sum_s f_s + 113 \int_0^{\lambda=I} \sigma_a(\lambda)/\lambda^2 d\lambda, \quad (4)$$

where the first term is the oscillator strength for the discrete spectrum and the second term applies to the ionization continuum, with I the ionization potential. σ_a is the total absorption cross section at wavelength λ . For an atom the absorption and ionization cross sections are identical at wavelengths shorter than the ionization threshold. Thus, we evaluated the continuum oscillator strength from the ionization threshold, 910 Å, down to 120 Å using the present data and from 120 to 0 Å from the compilation by Henke *et al.*³⁰ The results were 4.58 and 2.58, respectively, yielding a total continuum f value of 7.16. The problem now is to determine the contribution from discrete lines. f values of several discrete lines, including autoionizing transitions, have been measured by many groups.^{6,32–37} A critical compilation of the data has been given by Wiese *et al.*³⁸ We have selected all the allowed absorption transitions from these compilations along with the data reported by Dehmer *et al.*⁶ and obtain $\sum f_s = 0.71$. This gives a total oscillator strength of 7.87, which is only 1.6% less than the required

value of 8. Of course, there will be a small contribution from the remaining discrete transitions still to be analyzed.

Although the uncertainty of the line oscillator strengths, quoted by Wiese *et al.*, are 25% to 50% this only alters the final total oscillator strength by a few percent. Thus, the above analysis of the total oscillator strength provides a self-consistent check on the accuracy of the present data.

Figure 5 compares our experimental results (solid circles) with the theoretical calculations of Starace *et al.*,¹⁶ Taylor and Burke,¹⁷ and with Pradhan.¹⁹ The data of Starace *et al.* (solid line) were derived by use of Herman-Skillman (HS) wave functions. These calculations do not include any electron correlation effects. The agreement with the experimental data is extraordinary. There is precise agreement in shape and magnitude with experiment from 120 to 500 Å and less than 10% deviation from 500 Å to the $^2D^o$ threshold at 731.8 Å.

In contrast, the calculations of Taylor and Burke (dashed line) used the more rigorous *R*-matrix method. They point out that all channels associated with the main final states along with all channels of the initial state (viewed as a bound state of the electron-plus-ion system) were included in their cross section calculation. Thus, in addition, they were able to calculate the positions and shapes of many autoionizing lines. Their results (dipole length) are nearly identical to the HS calculations from the $^2P^o$ threshold to shorter wavelengths. Their agreement with experiment from threshold to 400 Å is even better including their prediction of the $2s2p^4(^4P)3p(^3D^o, ^3S^o, ^3P^o)$ autoionizing lines. They predict, in agreement with experiment, the slow rise in cross section nearly 20 Å away from the peak shown in Fig. 5 by the dashed line. They also predict the peak posi-

tion of the resonance lines to occur at 479.3 Å, 477.6 Å, and 475.6 Å. The position of the observed resonance can be estimated only from the partial coincidence with the resonance of an emission line from our light source at 479.43 Å. Taylor and Burkes' results near the $^4S^o$ threshold are shown in the dipole length (short dashes) and dipole velocity (long dashes) approximations. At threshold their cross sections are 4.1 and 3.4 Mb, respectively.

The calculations by Pradhan¹⁹ (crosses) and earlier by Pradhan and Saraph¹⁸ also used the close-coupling approximation with correlations in both the initial and final states. However, there are slight differences in the number and types of channels included in their calculations compared to those of Taylor and Burke. Again the agreement with the present data is very good except near the $^2P^o$ threshold. They have calculated the positions of many autoionizing resonances. We reproduce their cross sections before and after the $3p(^3D^o, ^3S^o, ^3P^o)$ resonance to show the agreement with Taylor and Burke and with experiment.

The good agreement between the HS and close-coupling calculations with the experimental results suggests that correlation effects are not too important in calculating the total photoionization cross sections of atomic oxygen, except near thresholds, where we observe some discrepancies, and in predicting the shape and positions of autoionizing structure. However, good calculations that only partially take into account correlations show poorer agreement with the present data, at least from threshold down to about 450 Å. Towards shorter wavelengths most of the calculations agree with experiment.

The major remaining discrepancy between theory and experiment is the shape and magnitude of the cross section between the $^2P^o$ threshold and the first resonance line. It is possible that there is still some correlation lacking that might explain this peak in the cross section.

ACKNOWLEDGMENTS

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APPENDIX

Determination of $\sigma(O)$

When atomic oxygen is produced by a microwave discharge in O_2 the products of the discharge are primarily $O(^3P)$, $O_2(X^3\Sigma)$, and $O_2(a^1\Delta)$. Each of these species can be ionized in the spectral region of interest. In addition, both the $^3\Sigma$ ground state and the $^1\Delta$ excited state of O_2 produce atomic ions through the process of dissociative photoionization. The following analysis to determine the direct photoionization cross section of atomic oxygen $\sigma(O)$ takes into account the presence of these products.

From the Lambert-Beer law the number of ions of a given species that are produced per second is given by,

$$N = I_0 \sigma n l, \quad (A1)$$

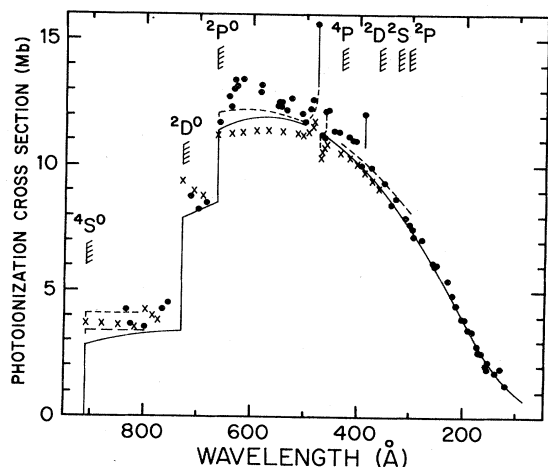


FIG. 5. Comparison of the absolute photoionization cross section of atomic oxygen with theoretical results. ●, present experimental data; ×, close-coupling calculations by Pradhan (Ref. 19); —, (excluding resonances), Herman-Skillman calculations by Starace *et al.* (Ref. 16); ---, dipole velocity and - · -, length approximations in the close-coupling calculations by Taylor and Burke (Ref. 17).

where I_0 is the incident number of photons/s, σ is the photoionization cross section for producing a specific ion, n is the number density of the neutral gas, and l is the path length from which the ions are collected. The above expression is true for $\sigma nl \ll 1$.

After the ions have passed through a mass spectrometer, of transmission T , and are detected by an electron multiplier the output signal S is given by

$$S = (I_0 \sigma nl) G \Gamma T e, \quad (\text{A2})$$

where G is the multiplier gain, Γ is the efficiency for secondary electron emission for a specific ion, and e is the electronic charge.

Applying Eq. (A2) to the detection of O^+ and O_2^+ ions under the conditions with the microwave generator switched *OFF* and *ON* (primed quantities) and letting the constant $C = lGe$ we obtain the following equations:

Microwave *OFF*

$$\text{O}_2^+: S_2 = (I_0 C) (\Gamma_2 T_2) \sigma_\Sigma n_\Sigma. \quad (\text{A3})$$

$$\text{O}^+: S_1 = (I_0 C) (\Gamma_1 T_1^D) \sigma_\Sigma^D n_\Sigma. \quad (\text{A4})$$

Microwave *ON*

$$\text{O}_2^+: S_2' = (I_0 C) (\Gamma_2 T_2) (\sigma_\Sigma' n_\Sigma + \sigma_\Delta' n_\Delta). \quad (\text{A5})$$

$$\text{O}^+: S_1' = (I_0 C) \Gamma_1 [T_1^D \sigma_\Sigma^D n_\Sigma' + T_1^D \sigma_\Delta^D n_\Delta' + T_1 \sigma(\text{O}) n'(\text{O})]. \quad (\text{A6})$$

The subscripts 1 and 2 refer to atomic and molecular properties, respectively, and the superscript D refers to dissociative ionization processes. For example, T_1^D represents the transmission through the mass spectrometer of the energetic atomic ions produced by dissociative photoionization and σ_Σ^D represents the dissociative ionization cross section for producing O^+ from O_2 in the ground $^3\Sigma$ state. The subscript Δ refers to O_2 in the excited $a^1\Delta$ state and $n_{\Sigma, \Delta}'$ represents the number densities of O_2 in their Σ and Δ states, respectively, when the microwave generator is on.

The total number density of molecular oxygen with the microwave off is n_Σ (only ground-state molecules present). With the microwave on some of the molecules are lost in producing atoms and some are excited into the $^1\Delta$ state. Thus, the new number density of molecules is given by,

$$n'(\text{O}_2) = n_\Sigma' + n_\Delta'. \quad (\text{A7})$$

The lost molecules are then represented by the quantity $[n_\Sigma - n'(\text{O}_2)]$.

The number density $n'(\text{O})$ of the atomic oxygen produced by the microwave discharge and appearing in the ion chamber must be twice the number of O_2 molecules that disappear in the ion chamber when the discharge is on. This will be true provided that any atoms formed in the flow tube and lost by wall recombinations or any other mechanism reform into O_2 . To check the validity of this assumption the mass spectrum was scanned with and

without the microwave discharge to search for new products, for example, O_3 . However, no additional products were observed. Thus,

$$n'(\text{O}) = 2[n_\Sigma - n'(\text{O}_2)]. \quad (\text{A8})$$

The following defined quantities help to simplify the above equations, namely,

$$\alpha = n'(\text{O}_2)/n_\Sigma, \quad (\text{A9})$$

$$2(1-\alpha) = n'(\text{O})/n_\Sigma, \quad (\text{A10})$$

$$\beta = n_\Delta'/n'(\text{O}_2). \quad (\text{A11})$$

First, eliminate $I_0 C$ from Eq. (A6) by use of Eq. (A3) and solve for $\sigma(\text{O})$, obtaining,

$$\sigma(\text{O}) = (S_1'/S_2) (\Gamma_2 T_2 / \Gamma_1) [n_\Sigma / n'(\text{O})] \sigma_\Sigma - T_1^D [n_\Delta' / n'(\text{O})] \sigma_\Delta^D - T_1^D [n_\Sigma' / n'(\text{O})] \sigma_\Sigma^D. \quad (\text{A12})$$

Factor out the quantity $[n_\Sigma / n'(\text{O})]$ and eliminate all number densities by use of Eqs. (A9), (A10), and (A11). Then Eq. (A12) becomes,

$$\sigma(\text{O}) = [1/2(1-\alpha)] [(S_1'/S_2) (\Gamma_2 T_2 / \Gamma_1 T_1) \sigma_\Sigma - (T_1^D / T_1) \alpha \beta (\sigma_\Delta^D - \sigma_\Sigma^D) - (T_1^D / T_1) \alpha \sigma_\Sigma^D]. \quad (\text{A13})$$

Although no measurement of σ_Δ^D has ever been made it is reasonable to estimate that it is of the same order of magnitude as σ_Σ^D , and each is $< \sigma_\Sigma$. Thus, $(\sigma_\Delta^D - \sigma_\Sigma^D) / \sigma_\Sigma$ will range from 0 to < 1 . From Fig. 2 we see that (T_1^D / T_1) ranges from 0.23 to 1. We estimate β to be ~ 0.01 to 0.05. α was typically 0.7 to 0.8. So, to a good approximation we can set the middle term to zero. Rearranging Eq. (A13) and eliminating terms in $(\sigma_\Sigma^D / \sigma_\Sigma)$ by use of Eqs. (A3) and (A6) we obtain a usable expression for the *absolute cross section*, namely,

$$\sigma(\text{O}) = [1/2(1-\alpha)] (\Gamma_2 T_2 / \Gamma_1 T_1) [(S_1' - S_1 \alpha) / S_2] \sigma_\Sigma. \quad (\text{A14})$$

The relative cross section can be obtained from Eq. (A14) by noting that (S_2 / σ_Σ) is proportional to the absolute intensity I_0 of the incident radiation, see Eq. (A3). Further, from the definition of the photon detector efficiency η , namely,

$$\eta = (i_{\text{ph}} / e) / I_0, \quad (\text{A15})$$

where i_{ph} is the detector signal in amperes and e is the electronic charge, we see that

$$I_0 \propto i_{\text{ph}} / \eta. \quad (\text{A16})$$

Substituting into Eq. (A14) we obtain the *relative cross section*, namely,

$$\sigma(\text{O}) \propto (\eta / i_{\text{ph}}) (S_1' - \alpha S_1). \quad (\text{A17})$$

Only the relative value of the detector efficiency η_r is required in Eq. (A17) and this can be found as a function of wavelength in a separate and independent experiment. When neon gas is used in the mass spectrometer we obtain the relation,

$$i_{\text{ph}}/\eta_r \propto I_0 \propto S(\text{Ne}^+)/\sigma(\text{Ne}), \quad (\text{A18})$$

where $\sigma(\text{Ne})$ is the known cross section of Ne and $S(\text{Ne}^+)$ is the output signal of the electron multiplier that measures the Ne^+ ion current.²⁹ The value of α can be found in terms of measurable quantities by use of Eqs. (A3) and (A5) and from the definitions of α and β . Solving for S'_2/S_2 we obtain,

$$S'_2/S_2 = \alpha[1 + \beta(\sigma_{\Delta} - \sigma_{\Sigma})/\sigma_{\Sigma}]. \quad (\text{A19})$$

The quantity β is the fraction of the molecules that are in the excited $^1\Delta$ state. Typically, β lies between 0.01 and 0.1.²³⁻²⁵ Further, the cross section of most diatomic mol-

ecules in the ionization continuum are similar, with the fractional differences varying between zero and $\pm 30\%$ between 120 and 700 Å. For the isoelectronic molecules CO and N_2 the variation lies between 0% and 16%.³¹ Thus, we would not expect the cross sections of such similar molecules as $\text{O}_2(^3\Sigma)$ and $\text{O}_2(^1\Delta)$ to show a larger deviation. Consequently, we take

$$\alpha = S'_2/S_2. \quad (\text{A20})$$

This should introduce less than 1% error in α . However, this assumption is not valid where autoionizing structure is present.

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