Absolute cross section for photoionization of atomic oxygen

J. L. Kohl, G. P. Lafyatis, H. P. Palenius,* and W. H. Parkinson
Center for Astrophysics, Harvard College Observatory and Smithsonian Astrophysical Observatory, Cambridge, Massachusetts 02138
(Received 2 November 1977)

The absolute cross section for photoionization of atomic oxygen from the $2p^4\,^3P$ ground state of O^0 to the $2p^3\,^4S$ ground state of O^+ has been measured at five narrow wavelength intervals between 89.8 and 76.2 nm. The cross section near the $2p^3\,^4S$ threshold is 4.5 Mb $\pm$ 7%. Recent calculations by Taylor and Burke, and by Pradhan and Saraph are in reasonable agreement with this work. The dipole-length results of Taylor and Burke (4.1 Mb) are in better agreement with the experiment than their dipole-velocity results (3.2 Mb).

Photoionization of atomic oxygen O^0 by extreme ultraviolet radiation from the sun is the primary process for the production of energetic electrons and ions in the daytime thermosphere,[1,2] and photoelectrons from O^0 provide the major source of electron heating in the daytime midlatitude ionosphere.[3] Photoionization is important in maintaining the ionization balance of O in H II regions[4] and in stellar atmospheres.[5] This paper reports new measurements of the absolute cross section for photoionization from the $2p^4\,^3P$ ground state of O^0 to the $2p^3\,^4S$ ground state of O^+. Two earlier measurements differ from each other by about a factor of 2.[6,7] Accurate theoretical calculations for many-valence-electron systems such as O^0 are more complicated than those for nearly closed-shell systems because there are usually more final-state channels which are important. The recent calculations of O^0 photoionization by Taylor and Burke[8] using the R-matrix method and by Pradhan and Saraph[9] using close-coupling configuration interaction are the first to provide a consistent treatment of correlation effects in the initial- and final-state wave functions. The near-threshold results of these two calculations are in harmony with one another. Both give a cross section about 45% larger than an earlier calculation by Henry.[10]

The present photoabsorption measurements were made using 12 000-K shock-heated gases produced behind reflected shock fronts from initial test-gas mixtures of about 1% O_2 and 99% Ne. The shock tube was equipped with explosively driven optical shutters with an opening time of about 20 μs. This arrangement eliminated absorptive materials permitting measurements in the extreme ultraviolet. A background light source was flashed through the gas when the shutters opened and the amount of absorption was photographically recorded in a normal incidence spectrograph. The initial gas-mixture concentrations, the temperature, and pressure of the shock-heated gas were measured.

Details of the experimental apparatus are given elsewhere.[11] Improvements in the original apparatus include: the shortening of the openings in the moving shutters to reduce the exposure time for emission by the shock-heated gas, a double diaphragm mechanism to initiate highly reproducible shocks, enclosure of the sealing surfaces of the shutter mechanism in a He environment to ensure the elimination of unwanted absorption by atmospheric gases leaking by the shutters during their travel, the use of an Os-coated diffration grating, and the addition of a light source similar to that of Balloffet, Romand, and Vodar (BRV)[12] as modified by Garton *et al.*,[13] and Cantù and Tondello[14] with a toroidal mirror assembly.[15] Our use of the BRV source using a polyethylene anode cap was recently described by Kühne and Kohl.[16]

Our determination of the total absorption cross section uses measured values of the transmittance of the shock-heated gas I/I_0 and the column densities of absorbers in the Lambert-Beer formula. I/I_0 was determined photographically with Kodak 101.01 film. Each film was calibrated with single flashes of the BRV source through mesh filters of various transmissions which were placed in the optical path of the absorption apparatus. The transmitted radiation from the BRV source was much greater than the thermal emission from the shock-heated gas so the latter could be ignored. The flash-to-flash reproducibility of the lamp was better than $\pm$5%.[16]

Two temperature measurements were made using the brightness emissivity method[17] with the $2p^3\,3s\,{}^5S^0$-$2p^3\,3s\,{}^5P$ line of O^0 at 777.2 nm and with the $2p^5\,(^2P^o_{3/2})3s\,[1\tfrac{1}{2}]^0$-$2p^5(^2P^o_{3/2})3p\,[2\tfrac{1}{2}]$ line of Ne^0 at 640.2 nm. Pressure measurements were made using a piezoelectric pressure transducer. Local thermodynamic equilibrium (LTE) was assumed and the population densities of the species present were calculated using the Saha-Boltzmann equation, the ideal gas equation, and the plasma neutrality condition. At the thermodynamic conditions used for these measurements, much less than 1% of the O remains as O_2. Inelastic electron scatter-

ing will rapidly quench any overpopulation of O^0 metastable states formed from the dissociation of O_2. About 25% of the O exists as O^+. Although the Ne remains primarily in the ground state of Ne^0, the 1% Ne^+ contributes a large portion of the electron density. The geometrical path length through the shock tube was 7.24 cm. The effective path length was 6% larger because of gas which flows through the shutter holes during the measurements.[11]

Although the vacuum was maintained at a level in which the preshock gas densities of impurity species are expected to be less than 1% of the O^0 density, two contaminants C^0 and H^0 were identified in the high-temperature gas. The presence of C^0 was determined by examining the continuous absorption spectrum near the ground-state photoionization threshold of C^0 at 110 nm. Atomic carbon constituted a number density that was 4% of the O^0 density (0.08% of the total atomic density). The apparent cross section was corrected for the absorption by C^0 using the variation with wavelength of the photoionization cross section of C^0 as calculated by Taylor and Burke.[8] By photoelectrically examining $n = 3$-2 emission of H^0 from our usual O and Ne mixture and comparing to emission from a shock-heated gas of known H concentration, it was determined that the density of the H^0 impurity was about 6% of the O^0 density and a correction was made for this effect. To determine whether O^0 was present, in addition to the amount introduced, shock-heated gases were produced in the usual way except that O_2 was replaced with H_2. The O^0 line at 777.2 nm was monitored and the density of any O^0 contaminant was determined to be less than 1% of the usual density.

For wavelengths shorter than 82.8 nm it is possible for O^0 in the $2p^4\,{}^1D$ level to photoionize in the reaction

$$O^0(^1D) + h\nu \rightarrow O^+(^2D^o) + e^- .$$

Since about 6% of the O^0 are in the $2p^4\,{}^1D$ state, a correction was necessary which was based on the calculated cross section of Henry.[18] The similar corrections for photoionization from the $2p^4\,{}^1S$ and higher states are negligible.

Previously the apparatus was used to measure the photoionization cross section of H^0.[11] To test our procedures, this cross section was remeasured and the results, together with the theoretical values,[19,20] are shown in Fig. 1. Excellent agreement is obtained. Our procedures and analysis including the assumption of LTE are expected to be valid because of the agreement of the H^0 results with well-established theory. We expect the equilibrium behavior of shock-heated gases of O and Ne to be similar to those of H and Ne in the same concentrations. Non-LTE populations may result if electron collisions do not dominate radiative processes. Estimates based on the measured excitation rates[21] of O^0 suggest that the high electron densities together with the optical thickness of the shock-heated gas in the resonance lines of O^0 will lead to a near-Boltzmann population of states. The assumption of LTE is strengthened by the 2% agreement of the Ne^0 and O^0 temperature measurements.

Atomic-oxygen photoionization cross-section measurements with about 12 000-K gases were made in four trials. The following parameters of trial 1 were similar to the other three: 12 000-K temperature, 2500-torr total pressure, 3.47×10^{16}-cm^{-3} population density of the $2p^4\,{}^3P$ state of O^0, 1.76×10^{16}-cm^{-3} electron density, and 0.28 transmittance at 86.5 nm. The results of these measurements are summarized in Table I and Fig. 2. Measurements were made for five narrow wavelength intervals between 89.8 and 76.2 nm. Care was taken to avoid wavelength regions containing either lines in the BRV light source or resonant features in the photoabsorption of O^0, C^0, and Ne^0.

To further test the assumption of LTE, one measurement was made using different thermodynamic conditions since we would expect the measured cross section to change if the LTE assumption were invalid. Trial 5 of Table I with a temperature of 9900 K and $O^0(2p^4\,{}^3P)$ density of 9.63×10^{16} cm^{-3} agrees within its slightly larger experimen-

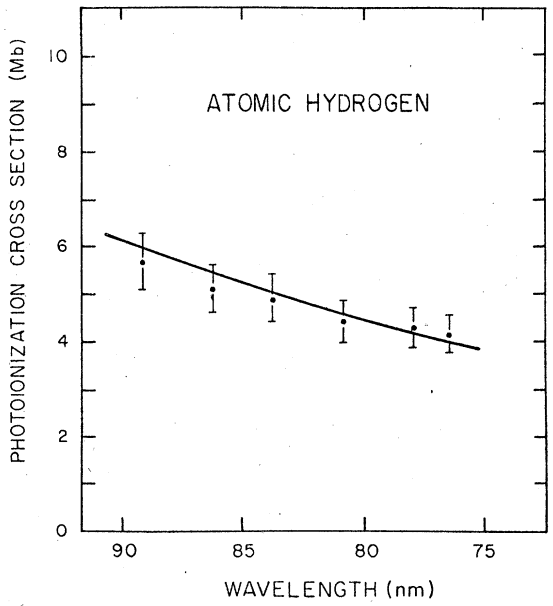

FIG. 1. Photoionization cross section of atomic hydrogen. The present measurements are designated by solid circles and the well-established theoretical values with the curve.

TABLE I. Results for cross section σ for photoionization from $O^0(2p^4\,^3P)$ to $O^+(2p^3\,^4S)$.

Wavelength (nm)	Wavelength interval (nm)	σ from trial 1 (Mb)	σ from trial 2 (Mb)	σ from trial 3 (Mb)	σ from trial 4 (Mb)	Mean cross section for trials 1–4 [a] (Mb)	Fluctuations Among trials [b]	σ from trial 5 (Mb)
89.5	0.6	4.29	5.13	3.90	4.82	4.54 ± 7%	±12%	3.96
86.5	0.4	4.04	4.83	3.53	4.67	4.27 ± 7%	±14%	4.29
84.0	0.6	4.71	5.60	4.32	5.42	5.01 ± 7%	±12%	4.49
78.0	0.4	4.59	5.64	4.29	4.93	4.86 ± 9%	±12%	4.80
76.5	0.5	5.30	4.98	5.27	5.66	5.30 ± 9%	± 5%	

[a] Uncertainties represent most probable error in mean values from sources listed in Table II.
[b] One standard deviation, trial 5 not included.

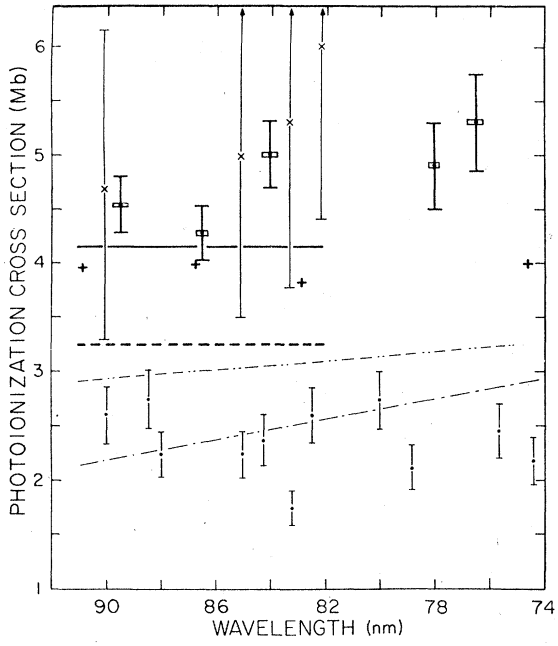

FIG. 2. Present state of knowledge regarding the absolute cross section for continuous photoionization of atomic oxygen for photon wavelengths between the $2p^3\,^4S$ threshold and 74.0 nm. Experimental values include the present work (rectangles), measurements of Cairns and Samson, Ref. 6 (crosses) and of Comes, Speier, and Elzer, Ref. 7 (dots). Theoretical values include the R-matrix results of Taylor and Burke, Ref. 8 (length, line; velocity, dashed curve), close-coupling configuration-interaction calculations by Pradhan and Saraph, Ref. 9 (crosses), and earlier calculations by Henry, Ref. 10 (length, dash-dot-dotted curve; velocity, dash-dotted curve).

tal uncertainty with the measurements made on the 12 000 K gases.

The sources of uncertainty are summarized in Table II, where we have identified sources of uncertainty in the column densities and in the transmittance of the shock-heated gas. Independent uncertainties that do not vary from trial to trial are designated as systematic.

We estimate the most probable error for a single trial to be ±11% and ±13% for wavelengths longer and shorter than 82.8 nm, respectively. The observed fluctuations given in Table I support this estimate. The error bars in Fig. 2 represent the most probable errors for the mean values of trials 1–4, where the contributions of random errors listed in Table II have been reduced by the square root of the reciprocal of the number of trials.

Comparing our results with other experimental values using Fig. 2, we find that the ±7% uncertainty limits of this work fall within the ±30% un-

TABLE II. Sources of uncertainty.

Source	% uncertainty in nl Systematic	Random	Source	% uncertainty in I/I_0 Systematic	Random
Initial mixture	1	<1	Variations in BRV	•••	5
Pressure	2	3	Absorption of C^0	3	8
Temperature	1	2	Absorption of H^0	<1	1.5
Calculations	2	•••	Photographic variations	•••	5
Shock-tube dimension	<1	•••	Characteristic curve interpolation	1	5
Gas through holes	3	•••	Mesh filter	0.5	•••
			Photographic granularity	•••	<0.3
			Absorption from $O^0(^1D)$ (for $\lambda < 82.8$ nm)	6	

certainties of Cairns and Samson[6] but the values of Comes, Speier, and Elzer[7] are about six most probable error intervals smaller than the present values. The discrepancy can not be reconciled in view of the respective error limits. Of the theoretical predictions, the dipole-length values of Taylor and Burke[8] agree best with our measurements although their results with the velocity formulation are significantly smaller than our experimental values, especially for wavelengths shorter than 85.0 nm. The calculations of Pradhan and Saraph[9] predict cross sections approximately equal to those of Taylor and Burke. Earlier theoretical predictions by Henry[10] fall well outside our experimental uncertainties. The more recent calculations[8,9] show the importance of correlation effects not included in the earlier work of Henry. Henry used a Hartree-Fock wave function for the initial state and a close-coupling wave function for the continuum state. Taylor and Burke, and Pradhan and Saraph use more complete close-coupling solutions to describe the ground state of the neutral as well as the final state of the ion-plus-electron system so that correlation effects are treated similarly in initial and final wave functions.

The more rigorous treatments of the problem by the recent two calculations have markedly improved the agreement between theory and our experiment. Agreement with the length formulations now is at about the ±15% level. A detailed study of the convergence of the calculations may indicate if the expected uncertainty of the theoretical values would explain the remaining disagreement with experiment.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the participation of W. E. Millikin, Jr., in the scientific measurements and his comments on the manuscript. We thank G. A. Victor for helpful discussions and comments. This work was supported by NASA under Grant No. NGL 22-007-006 and by the Smithsonian Institution.

*Present address: University of Lund, Lund, Sweden.

[1]M. Oppenheimer, E. R. Constantinides, K. Kirby-Docken, G. A. Victor, A. Dalgarno, and J. H. Hoffman, J. Geophys. Res. (to be published).
[2]G. A. Victor, K. Kirby-Docken, and A. Dalgarno, Planet. Space Sci. 24, 679 (1976).
[3]L. H. Brace, W. R. Hoegy, H. G. Mayr, G. A. Victor, W. B. Hanson, C. A. Reber, and H. E. Hinteregger, J. Geophys. Res. 81, 5421 (1976).
[4]R. M. Hjellming, Astrophys. J. 143, 420 (1966).
[5]E. Chipman, Smithsonian Astrophysical Observatory Special Report No. 338 (1971).
[6]R. B. Cairns and J. A. R. Samson, Phys. Rev. 139, A1403 (1965).
[7]F. J. Comes, F. Speier, and A. Elzer, Z. Naturforsch. 23a, 125 (1968).
[8]K. T. Taylor and P. G. Burke, J. Phys. B 9, L353 (1976).
[9]A. K. Pradhan and H. E. Saraph, J. Phys. B 10, 3365 (1977).
[10]R. J. W. Henry, Planet. Space Sci. 15, 1747 (1967).
[11]H. P. Palenius, J. L. Kohl, and W. H. Parkinson, Phys. Rev. A 13, 1805 (1976).
[12]G. Balloffet, J. Romand, and B. Vodar, C. R. Acad. Sci. 252, 4139 (1961).
[13]W. R. S. Garton, J. P. Connerade, M. W. D. Mansfield, and J. E. G. Wheaton, Appl. Opt. 8, 919 (1969).
[14]A. M. Cantù and G. Tondello, Appl. Opt. 14, 996 (1975).
[15]R. A. Roig and G. Tondello, J. Phys. B 9, 2373 (1976).
[16]M. Kühne and J. L. Kohl, Appl. Opt. 16, 1786 (1977).
[17]W. H. Parkinson and E. M. Reeves, Proc. R. Soc. A 282, 265 (1964).
[18]R. J. W. Henry, Astrophys. J. 161, 1153 (1970).
[19]R. W. Ditchburn and U. Öpik, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic, York, 1962), p. 79.
[20]W. J. Karzas and R. Latter, Astrophys. J. Suppl. Ser. 6, 167 (1962).
[21]E. J. Stone and E. C. Zipf, J. Chem. Phys. 60, 4237 (1974).