Photodissociation and photodetachment of molecular negative ions. VI. Ions in O_2/CH_4/H_2O mixtures from 3500 to 8600 Å

L. C. Lee, and G. P. Smith

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Molecular Physics Laboratory, SRI International, Menlo Park, California 94025
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The photodestruction cross sections for O^-, O_2^-, $O_2^-\cdot H_2O$, O_3^-, $O_3^-\cdot H_2O$, O_4^-, OH^-, and OD^- have been measured in the 3500–5400 Å and 6300–8600 Å wavelength regions. The ions were produced in a drift tube mass spectrometer and interacted with a dye laser or ion laser inside the laser cavity. The photodetachment cross sections for O^- and $OH^-(OD^-)$ have sharp onsets at wavelengths near 8480 and 6795 Å, respectively, and at shorter wavelengths their values are nearly constant. The photodestruction cross sections for O_2^-, O_4^-, and $O_2^-\cdot H_2O$ increase monotonically with increasing photon energy. In contrast, in the photodestruction cross section for O_3^-, structure is observed over this wavelength region. The processes for creation and photodestruction of the various negative ions are discussed. Comparison is made with other measurements.

I. INTRODUCTION

Within the last few years the photodissociation and photodetachment cross sections for many negative[1-5] and positive[6,7] ions have been measured in our laboratory. These cross sections are important for modeling the charge density in the D region of the ionosphere.[8] As an example, the photodestruction cross sections for CO_3^-, $CO_3^-\cdot H_2O$, and O_3^- have been used to explain the rapid increase of electron density in the D region of the ionosphere at sunrise.[9]

The photodestruction cross sections of ions are of fundamental interest for several reasons. The vibrational frequencies of negative ions have been determined[10-12] from the structure observed in the photodestruction spectra;[2,3,12] the electron affinities of neutral parent molecules have been obtained from the thresholds of photodetachment cross sections[13-15]; and the repulsive states of ions have been established from the dissociation continua.[7,16]

In this paper, we report the photodestruction cross sections for various ions formed in mixtures of O_2, CH_4, D_2, and H_2O over the wavelength regions 3500–5400 and 6300–8600 Å. These cross sections have been previously examined at various wavelengths by several investigators.[1-5,13,14,17-21] However, few measurements are available for the wavelength regions of interest here. The results of our measurements are compared with others.

II. EXPERIMENTAL

The experimental apparatus used for our measurements has been described in some detail in several previous publications.[1-3] Briefly, a drift tube mass spectrometer apparatus was used as the ion source, drift region, mass analyzer, and ion detector. The source and drift regions were filled with the gas of interest at a pressure of 0.05–0.5 Torr. The negative ions were formed in the gas phase by electron attachment processes and by subsequent ion–molecule reactions. Under the influence of a weak uniform electric field, the ions drifted toward a 1 mm-diameter exit aperture. The ratio of the applied electric field to the neutral gas density, E/N,

was limited to 10 or 20 Td (1 Td = 10^{-17} V-cm²); thus, the ion drift velocity was only about one-tenth the mean thermal speed of the ions and neutral molecules at room temperature. The drift distance, which could be varied over a range of 2.5–50.8 cm, was chosen so that the ions experience many thermalizing collisions after their production and are essentially in thermal equilibrium[16] with the neutral molecules at 300 K.

The drifting ions intersect a laser beam of ~1.5 mm diameter in front of the exit aperture. The light source in the near infrared region was a dye laser pumped by the 6471 and 6764 Å lines of nominal 4 W krypton ion laser. The dyes[22] used were rhodamine 640 perchlorate for the 6200–6950 Å region, oxazine 1 perchlorate for 6950–7900 Å, and 3-3'-diethyloxatricarbocyanine iodide (DEOTC) for 7700–8600 Å. In the short wavelength region, various lines of the Ar^+ and Kr^+ ion lasers were used. The laser lines were tuned by a prism, except the ultraviolet line from the Kr^+ ion laser. The UV line consists of 66% 3507 Å and 34% 3569 Å. The interaction region of the laser with the ions was inside the dye laser cavity, and the laser polarization was perpendicular to the ion drift velocity. The intracavity laser power varied from 5 to 100 W for the various wavelengths. The ions of interest were selected by a quadrupole mass spectrometer and detected by an electron multiplier. The laser was mechanically chopped at 100 Hz. The ions were counted for equal periods during which the laser was on and off. The cross sections were placed on an absolute scale by normalization to negative ions for which the photodestruction cross sections are known. The mobilities, K_0, and the ions chosen for normalization are listed in Table I. The mobilities are adopted from published values[23] or are scaled[20,23] from masses of the ion and gas molecules.

The distance and the gas pressure were chosen to optimize the concentration of ions of interest and to minimize the interference from other species in the drift tube. The gas mixtures and the gas pressures are listed in Table I. The density of ions in the drift tube was kept low so that the cross section measurements were not significantly affected by secondary processes such as mutual repul-

TABLE I. Experimental conditions of the mobilities K_0, and the ions chosen for normalization.

Ion	Gas	Pressure (Torr)	Normalized to	K_0 (cm^2/V sec)
D$^-$	D$_2$	0.1, 0.2		30.0
O$^-$	O$_2$	0.1	D$^-$ in D$_2$, O$_2^-$ in O$_2$	3.20
O$_2^-$	O$_2$	0.2	O$^-$ in O$_2$, D$^-$ in D$_2$	2.16
O$_2^-\cdot$H$_2$O	O$_2$/trace H$_2$O	0.4	O$_2^-$ in O$_2$	2.58
O$_3^-$	O$_2$	0.4	O$_2^-$ in O$_2$	2.56
O$_3^-\cdot$H$_2$O	O$_2$/trace H$_2$O	0.4	O$_2^-$ in O$_2$	2.20
O$_4^-$	O$_2$	0.4	O$_2^-$ in O$_2$	2.08
OH$^-$	O$_2$, 2% CH$_4$	0.2	O$^-$ in O$_2$	3.18
OH$^-$	He, 2% O$_2$, 1% CH$_4$	0.2	O$^-$ in He	20.2
OD$^-$	O$_2$, 2% D$_2$, 2% CH$_4$	0.2	O$^-$ in O$_2$	3.16

sion. The percentage of ions photodissociated was limited to less than 15% of the ions of interest by adjusting the dye laser power. This low destruction rate minimizes the effect of the ion diffusion (from the noninteraction region into the photon interaction region) on the measured cross section. This effect has been discussed in detail in a previous paper.[6]

At each wavelength the number of ion counts was accumulated until the statistical uncertainty in the photodestruction signal was less than 10%. The statistical uncertainties are indicated by error bars along with the data shown later. The laser power and the ion mobility are known to within 5% of their true values. Including the uncertainty in the normalization procedure, the experimental uncertainty for the absolute photodissociation cross sections is estimated to be ±20%.

III. RESULTS AND DISCUSSION

A. O$^-$

All previous measurements of photodestruction cross sections for ions made in drift tubes have been normalized[1-7,20,21] to the photodetachment cross section of the O$^-$ ion. However, the absolute cross section for this ion has been measured only in a beam apparatus using broadband wavelength selection[14,19] of the photons. Detailed measurements on the photodetachment cross section of O$^-$ at high resolution are of great interest, especially at the threshold where the cross section has a sharp onset.

The photodetachment cross section of the H$^-$ ion is an attractive candidate for the normalization standard. This cross section has been extensively investigated both theoretically[24-28] and experimentally.[29,30] Representative results are plotted in Fig. 1. As indicated in this figure, the data given by various investigators are in good agreement, with a variation at each wavelength of less than 10%. The relative H$^-$ cross section measured by Smith and Burch[29] was put on an absolute scale by normalization to the theoretical calculations of Geltman.[24] The experimental uncertainties are estimated to be 10% for the measurements of Smith and Burch[29] and 8% for Popp and Kruse.[30] The mean values of all the experimental and

theoretical data shown in Fig. 1 are adopted for the normalization standard.

In the current measurement, the photodetachment cross section for O$^-$ was normalized to D$^-$, instead of H$^-$. This is because (i) H$^-$ has higher mobility[31] than D$^-$ so that the percentage of the H$^-$ ions destroyed by the laser is smaller than that of D$^-$ at the same laser power, and (ii) H$^-$ is harder to form and detect in the drift tube than D$^-$. Both isotopes are expected to have the same photodetachment cross section at each wavelength, because they have the same electronic structure and their wave functions differ only by the electron reduced mass ($\frac{1}{1840}$). The photodetachment cross section of O$^-$ normalized to D$^-$ is shown in Fig. 2 for the wavelength region from 6300 to 8600 Å. The error bar indicates the statistical uncertainty. The

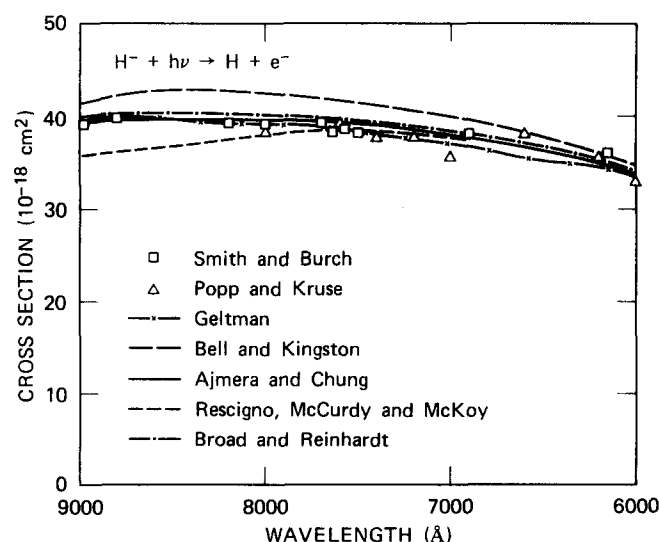FIG. 1. The photodetachment cross section for H$^-$ in the wavelength region 6000–9000 Å. Calculations were done by Geltman (Ref. 24), Bell and Kingston (Ref. 25), Ajmera and Chung (Ref. 26), Rescigno et al. (Ref. 27), and Broad and Reinhardt (Ref. 28). Measurements were made by Smith and Burch (Ref. 29) and Popp and Kruse (Ref. 30). The relative measurements of Smith and Burch were placed on an absolute scale by Geltman.
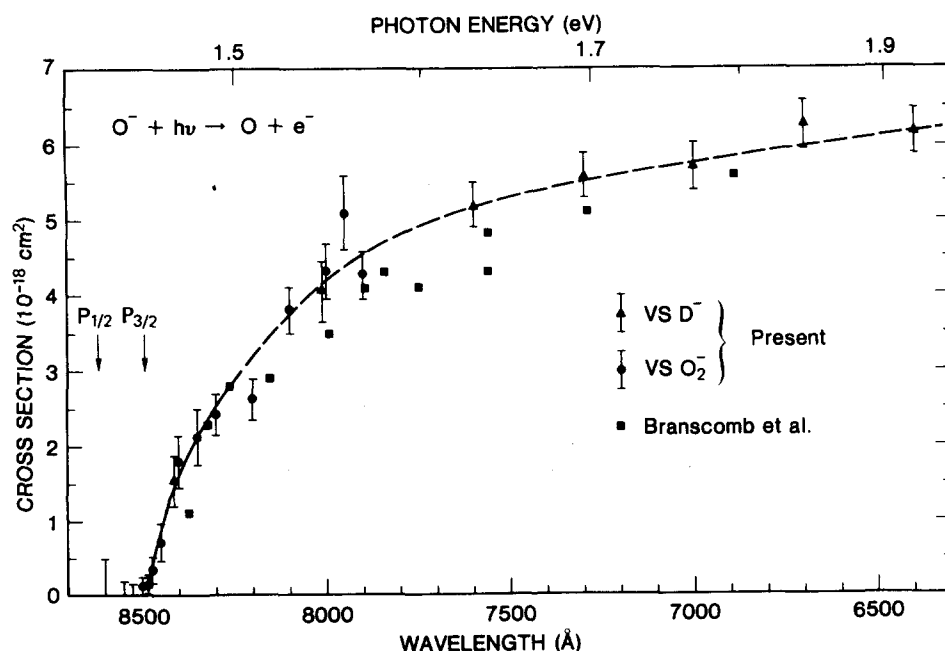
FIG. 2. The photodetachment cross section for O⁻ in the wavelength region 6300–8600 Å, placed on an absolute scale by normalization to D⁻ and O_2^-. The measurements of Branscomb *et al.* (Ref. 14) are included for comparison. The cross section near the second threshold (8480 Å) is fit by a a threshold law, which is indicated by the solid line. The thresholds for photodetachment of $O^*(^2P_{3/2})$ and $O^-(^2P_{1/2})$ are indicated. The dashed lines only serve to join the data. The error bars indicate experimental uncertainty.

D⁻ reduced mobility of $K_0 = (30.0 \pm 0.9)$ cm²/V-sec is adopted from Graham *et al.*[31]

To better define the rapid increase of the cross section in the threshold region, we measured the O⁻ cross section relative to O_2^-. In this wavelength region the O_2^- cross section, which is obtained by normalization to D⁻, shows a slow variation with wavelength (see next section). It is advantageous to normalize the O⁻ photodetachment cross section against O_2^- instead of D⁻, because O⁻ and O_2^- can be alternatively observed in the same parent gas, which minimizes experimental uncertainties such as variations in the laser–ion interaction region. The O⁻ cross section obtained by normalization to O_2^- is also shown in Fig. 2. These values are consistent with the data obtained by normalization to D⁻.

The earlier absolute cross sections of Branscomb *et al.*[14] measured with a bandwidth of 100 Å are also shown in Fig. 2. The experimental uncertainties are not given in Ref. 14, but from a previous paper[17] they may be estimated to be about 10%. The present measurements give values slightly higher than the data of Branscomb *et al.*,[14] but both measurements agree within their experimental uncertainties. Therefore, all the previous measurements in the visible region,[1-7,10,11,20] which have used the O⁻ photodetachment cross section of Branscomb *et al.*[14] as a normalization standard, are not substantially affected by the present results.

The data in Fig. 2 are joined together by the solid and dashed lines, which indicate the values to be used as a normalization standard for other ions. The dashed lines only serve to join the data points, but the solid line is fit by a threshold law, which is described as follows.

The dependence of the O⁻ photodetachment cross section on the wavelength near threshold has been discussed by Branscomb *et al.*[17] The ground state of O⁻ is ^2P, which has the configuration $(1s)^2(2s)^2(2p)^5$. In the photodetachment process one of the $2p$ electrons makes an

electric dipole transition to a continuum orbital, s or d. As indicated in Fig. 2, the O⁻ ion has two thresholds, depending on whether the ion is initially in the $^2P_{3/2}$ or $^2P_{1/2}$ state. The $O^-(^2P_{1/2})$ state has an energy[32] of 181 cm⁻¹ higher than $O^-(^2P_{3/2})$, so that its threshold energy is lower. As shown in Fig. 2, the apparent photodetachment cross section for the wavelengths between these two thresholds is very small. This is because in this wavelength region only the $O^-(^2P_{1/2})$ ions are photodetached. The concentration of O⁻ in the $^2P_{1/2}$ state is only about 20% of O⁻ in the $^2P_{3/2}$ state when estimated from a Boltzmann distribution at 300 K. At the $^2P_{3/2}$ threshold, λ_0, the photodetachment cross section has a sharp onset. The photodetachment cross section for wavelengths slightly shorter than this threshold is given[17] by

$$\sigma(\lambda) = \frac{\gamma}{\lambda}\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)^{1/2} + \frac{\gamma A_1}{\lambda}\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)^{3/2}, \tag{1}$$

where γ and A_1 are parameters to be determined from the experimental data.

For wavelengths in the 8300–8500 Å region, the experimental data are fit by $\gamma = 1.275 \times 10^{-23}$ cm⁷/² and $A_1 = 6.87 \times 10^{-5}$ cm, with $\lambda_0 = 8480$ Å as shown by the solid curve in Fig. 2. The first term in Eq. (1), which results from the transition to the s continuum orbital, is dominant. The uncertainty for λ_0 is ± 10 Å. The electron affinity of $O(^3P)$ determined from λ_0 is 1.462 ± 0.002 eV, which is identical to the value of 1.462 ± 0.003 eV recently recommended by Hotop and Lineberger.[32]

B. O_2^-

The photodetachment cross section of O_2^- has been previously measured by several authors.[2,3,13,19,20,33] In this paper, extended measurements at 3500–5000 and 7000–8400 Å are reported. The O_2^- cross section is obtained by normalization to O⁻ in O_2, except at 8400 Å where it is normalized to D⁻ in D_2. The results are plotted in Fig. 3, in which the measurements given by Cosby *et*
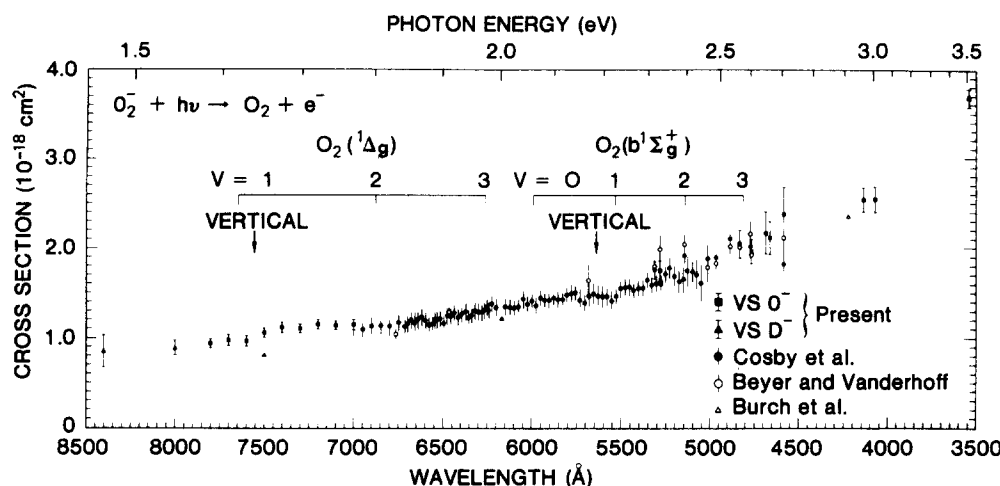
FIG. 3. The photodetachment cross section for O_2^- in the 3500–8500 Å region, placed on an absolute scale by normalization to D^- and O^-. The thresholds for photodetachment of O_2^- ($X^2\Pi$, $v=0$) into the various vibrational levels of $O_2(^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ are indicated. The vertical thresholds for photodetachment of O_2^- into these two electronic states are also shown. The measurements of Cosby et al. (Refs. 2 and 3), Burch et al. (Ref. 13), and Beyer and Vanderhoff (Ref. 20) are indicated for comparison.

al.,[2,3] Burch et al.,[13] and Beyer and Vanderhoff[20] are also shown. The present results agree very well with other measurements in the shorter wavelength region, but are slightly higher than those of Burch et al.[13] in the longer wavelength region. The data given by Warneck[19] in the 3000–6200 Å region and by Burt[33] at 4000–20 000 Å are not included in Fig. 3. Warneck's data are consistent with those of Burch et al.,[13] but Burt's data[33] are much higher than the present values. Burt's data are possibly affected by the improper normalization of the O_2^- cross section to O^- at high pressure, as discussed by Cosby et al.[2]

The photodestruction process in the present wavelength region can be definitely attributed to photodetachment. By combining the measured electron affinity for $O(^3P)$ of 1.462 ± 0.002 eV with the electron affinity for $O_2(X^3\Sigma_g^-)$ of 0.440 ± 0.008 eV[34] and the dissociation energy for $O_2(X^3\Sigma_g^-)$ of 5.1159 ± 0.0012 ev,[35] we obtain a dissociation energy for $O_2^-(X^2\Pi_g)$ of 4.094 ± 0.011 eV. Because the photon energy in the present region is less than 3.5 eV, only photodetachment is energetically possible.

In this wavelength region the photodetachment cross section of O_2^- does not depend on the drift distance, gas pressure, and laser power, but it does depend slightly on E/N, as shown in Fig. 4. Such E/N dependence has been reported previously.[2] At 5208 Å, the cross section decreases with higher E/N, but at 4131 Å, the cross section increases slightly with higher E/N. This is because O_2^- is effectively vibrationally excited by the applied electric field. The vibrationally excited states of O_2^- will have different transition probabilities from the ground state, so that the photodetachment cross section for O_2^- depends on the applied electric field. (Details of such effects are discussed elsewhere.)[36]

No prominent discrete structure is observed in the photodetachment cross section for O_2^-. This indicates that the photodetachment of O_2^- does not result from a preionization process. This result is consistent with the potential curves of O_2^- recently calculated by Das et al.[37] There is only one bound electronic excited state, $O_2^-(a^4\Sigma_u^-)$, energetically accessible at the present photon energies. However, the transition from the ground state, $O_2^-(X^2\Pi_g)$, to this excited state is optically forbidden, so that its os-

cillator strength is small. Therefore, the photodetachment cross section for O_2^- is not expected to have discrete structure in the present wavelength region.

The O_2^- cross section increases as the photon energy increases, as shown in Fig. 3. Burch et al.[13] have fit this increase over a wide range of photon energies by a threshold law

$$\sigma = A_0 \frac{1}{\lambda}\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)^{3/2} . \tag{2}$$

In fact, the threshold law is valid only in a small wavelength region (~200 Å for O^-). To justify their fitting, Burch et al.[13] have suggested that electron detachment is being observed from many vibrational levels of the $^4\Sigma_u^-$ state. According to the potential curves of Das et al.,[37] the $O_2^-(a^4\Sigma_u^-)$ state has an energy about 2 eV above $O_2(X^3\Sigma_g^-)$, and it is expected to have a short lifetime in the drift tube at a pressure of 0.4 Torr because it may undergo a collision-induced preionization to $O_2(X^3\Sigma_g^-)$. The preionization lifetime is expected to be short. For example, the preionization lifetime of $O_2^-(X^2\Pi_g, v=4)$ has
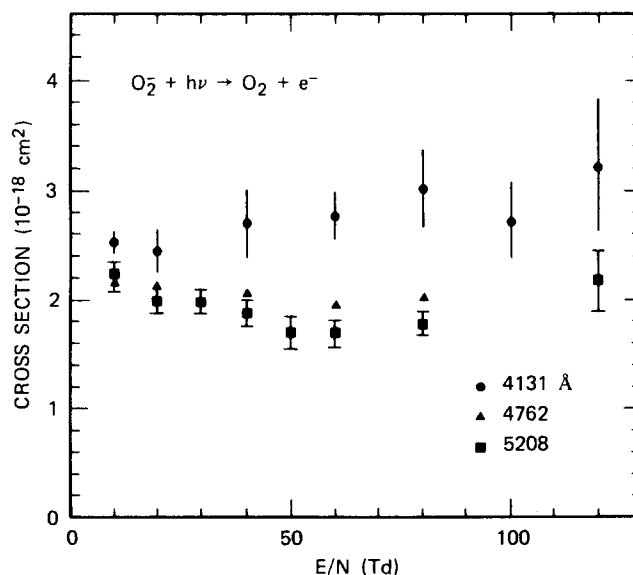

FIG. 4. The dependence of photodetachment cross section for O_2^- on E/N at the photon wavelengths 4131, 4762, and 5208 Å.

been estimated[38] to be $(1.0 \pm 0.3) \times 10^{-10}$ sec; the lifetime of higher levels is expected to be comparably short. Consequently, $O_2^-(a\,^4\Sigma_u^-)$ is not expected to exist in the drift tube. This is in accord with the inability to observe this state in the photoelectron spectrum[34] of O_2^-. The wavelength dependence of the O_2^- photodetachment cross section thus requires a new interpretation.

The 4880 Å photoelectron spectrum of O_2^-[34] indicates that the O_2^- ions are photodetached into every state in O_2 that is energetically accessible. The cross section for photodetachment of O_2^- into each state of O_2 may have a photon energy dependence similar to that for atomic photodetachment. That is, the photodetachment cross section[32] is nearly constant at photon energies more than ~ 0.1 eV above the photodetachment threshold, as is demonstrated by the O^- photodetachment cross section shown in Fig. 2. Each state of O_2 that is available for O_2^- to photodetach into will contribute to the photodetachment cross section. The photodetachment cross section for O_2^- will increase as the number of available states of O_2 increases. Thus, the photodetachment cross section for O_2^- will increase as the photon energy increases. This assertion is further supported by the fact that the rate of increase of the O_2^- photodetachment cross section changes at the thresholds for photodetachment of $O_2^-(X\,^2\Pi_g$, $v = 0$) into the various vibrational levels of $O_2(a\,^1\Delta_g, b\,^1\Sigma_g^+)$. The thresholds are calculated from the electron affinity[34] and the energies of electronic states[39] of O_2 and are indicated in Fig. 3. The vertical thresholds obtained from the $O_2^-(X\,^2\Pi_g)$ potential curve of Das et al.[37] are also indicated in Fig. 3. The rate of increase in the cross section changes only at photon energies higher than the vertical threshold. The changes are prominent at the vibrational thresholds.

C. $O_2^- \cdot H_2O$

The photodestruction cross section of $O_2^- \cdot H_2O$ has been measured by Cosby et al.[3] in the wavelength region 5200–6700 Å, by Smith et al.[5] in 7100–8250 Å, and by Vanderhoff[40] at 4100 Å. Extended measurements in the 3500–5400 Å region are reported in this paper and are shown in Fig. 5.

The $O_2^- \cdot H_2O$ ions were formed in the drift region by the reaction

$$O_4^- + H_2O \rightarrow O_2^- \cdot H_2O + O_2 \qquad (3)$$

with a rate constant[41] of 1.4×10^{-9} cm^3/sec. The O_4^- is formed by a three-body reaction[41] (see Sec. F).

The other process that forms $O_2^- \cdot H_2O$ is

$$O_2^- + H_2O + O_2 \rightarrow O_2^- \cdot H_2O + O_2 \ , \qquad (4)$$
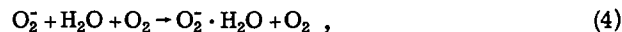
with a rate constant[41,42] of 3×10^{-28} cm^6/sec.

The bonding between a negative ion and a H_2O molecule is through a hydrogen bond.[43,44] The clusters of negative ions that have been studied theoretically, such as $F^- \cdot H_2O$,[43] $Cl^- \cdot H_2O$,[43] and $CN^- \cdot H_2O$,[44] are found to have the most stable structure when the negative ions and the hydrogen and oxygen atoms are collinear. Accordingly, the most stable structure for $O_2^- \cdot H_2O$ is likely to be
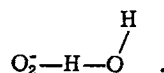
$$O_2^- - H - O \overset{\displaystyle H}{\diagup} \ .$$

The $O_2^- \cdot H_2O$ ion may be photodissociated by breaking the O_2^-–HOH bond with a dissociation energy of 0.8 eV.[45] It may also undergo dissociative photodetachment

$$O_2^- \cdot H_2O + h\nu \rightarrow O_2 + e + H_2O \ . \qquad (5)$$

The photodestruction cross section of $O_2^- \cdot H_2O$ shown in Fig. 5 has a wavelength dependence qualitatively similar to the photodetachment cross section of O_2^- shown in Fig. 3, except for a shift to the blue. The photodestruction process of $O_2^- \cdot H_2O$ is therefore most likely dominated by the dissociative photodetachment process (5). The threshold energy for process (5) will exceed the electron affinity of O_2 (0.44 eV)[34] by approximately the $O_2^- \cdot H_2O$ bond energy (0.8 eV).[45] The threshold energy for dissociative photodetachment $O_2^- \cdot H_2O$ into $O_2(X\,^3\Sigma_g^-, v = 0) + e + H_2O$ is thus estimated to be 1.24 eV. The apparent threshold for photodestruction of $O_2^- \cdot H_2O$ obtained by extrapolation of the cross section to zero is 1.8 ± 0.1 eV.[5] Additional energy is carried away by the photofragments.

Photodestruction of $O_2^- \cdot H_2O$ by the photodissociation process is energetically possible in the wavelength
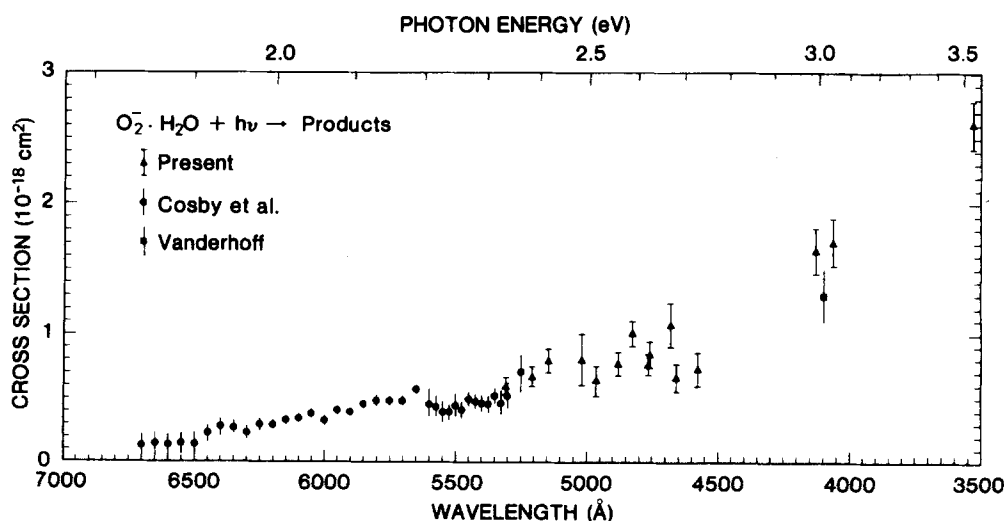

FIG. 5. The photodestruction cross section for $O_2^- \cdot H_2O$ in the 3500–6800 Å region. The measurements of Cosby et al. (Ref. 3) and Vanderhoff (Ref. 40) are indicated.
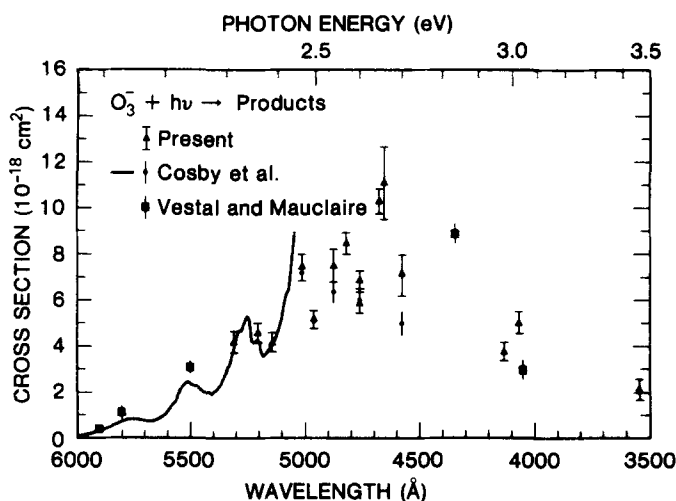
FIG. 6. The photodestruction cross section for O_3^- in the 3500–6000 Å region. The measurements of Cosby et al. (Refs. 2 and 3) and Vestal and Mauclaire (Ref. 47) are indicated.

region of interest. However, it is difficult to identify this process in the present experimental arrangement because any possible O_2^- photofragment signal is obscured by the large amount of O_2^- in the drift tube.

D. O_3^-

The photodestruction processes of O_3^- in the gas phase have been previously investigated by several authors.[2,3,11,12,46,47] O_3^- is formed by a three-body reaction[41,48]

$$O^- + 2O_2 \rightarrow O_3^- + O_2 \tag{6}$$

with a rate constant[41] of 1×10^{-30} cm^6/sec^{-1}.

The O_3^- ions can undergo photodetachment

$$O_3^- + h\nu \rightarrow O_3 + e^- \tag{7}$$

with a threshold at 2.1028 eV,[12,46] and can also undergo photodissociation

$$O_3^- + h\nu \rightarrow O^- + O_2 \tag{8}$$

or

$$O_3^- + h\nu \rightarrow O + O_2^- \tag{9}$$

with thermodynamic thresholds[2] at 1.7 ± 0.2 and 2.7 ± 0.2 eV, respectively.

In the photon energy range of interest, the photodissociation (8) is the dominant process.[3] The photodetachment process (7) has a cross section[46] less than 10% of the total photodestruction cross section.[2] The photodestruction cross section of O_3^- is shown in Fig. 6. The present measurements are shown together with the previous measurements[2,3] made at longer wavelengths. The cross sections for both processes (8) and (9) given by Vestal and Mauclaire[47] are also shown in Fig. 6 for comparison. In their measurements, the initial vibrational distribution of O_3^- is not known, and a large fraction of the O_3^- ions is expected to be in vibrationally excited states.

As shown in Fig. 6, the photodestruction cross section has discrete structure with maxima at about 5760,

5510, 5270, 5050, 4850, and 4660 Å. The structure at wavelengths longer than 5000 Å has been analyzed in detail by Cosby et al.[11] This structure is attributed to the transitions from the ground O_3^- state to the vibrational levels of a quasibound excited electronic state, which predissociate. The structure observed in this study at shorter wavelengths is a result of the same progression, because the separations between the primary maxima are about the same, ~ 820 cm^{-1}. The structure will be examined in detail in the near future using a tunable dye laser in this wavelength region.

E. $O_3^- \cdot H_2O$

The $O_3^- \cdot H_2O$ ions are formed by a three-body reaction,[42]

$$O_3^- + H_2O + O_2 \rightarrow O_3^- \cdot H_2O + O_2 \tag{10}$$
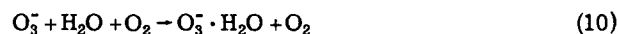
with a rate constant of 2.7×10^{-28} cm^6 sec^{-1}.

Similar to $O_2^- \cdot H_2O$, it is likely that O_3^- will be clustered through hydrogen bonding (~ 0.5 eV).[43–45] The photodestruction of $O_3^- \cdot H_2O$ in the present wavelength region is mainly attributable to the photodissociation processes,[4]

$$O_3^- \cdot H_2O + h\nu \rightarrow O_3^- + H_2O \tag{11}$$

and

$$O_3^- \cdot H_2O + h\nu \rightarrow O^- + O_2 + H_2O \ . \tag{12}$$

The cross section for the dissociative photodetachment process

$$O_3^- \cdot H_2O + h\nu \rightarrow O_3 + e + H_2O \tag{13}$$

is expected to be small, because the photodetachment of O_3^- is small compared to photodissociation (see Sec. D). In addition, $O_3^- \cdot H_2O$ photodetachment will take place only at wavelengths shorter than 4700 Å, because the threshold for photodetachment of $O_3^- \cdot H_2O$ is higher than the threshold for O_3^- (2.1028 eV)[12] by the bond energy of $O_3^- \cdot H_2O$ (~ 0.5 eV).

The photodestruction cross section of $O_3^- \cdot H_2O$ is shown in Fig. 7, along with the previous measurements[4] at longer wavelengths. In the previous measurements, discrete structure similar to that shown in O_3^- has been observed.[4] However, extension of this structure is not apparent in the present measurements. The laser wavelengths currently used may be too few to illustrate this structure. Further investigation of the structure using a tunable dye laser is planned.

F. O_4^-

O_4^- ions are formed from O_2^- by the three-body reaction

$$O_2^- + O_2 + O_2 \rightleftharpoons O_4^- + O_2 \ . \tag{14}$$

The rate constants[41] for the forward and reverse reactions are 4×10^{-31} cm^6/sec and 2.7×10^{-14} cm^3/sec, respectively. The O_4^- ions are created all along the drift region, and the ions created in the region near the laser beam may be vibrationally excited.[5]

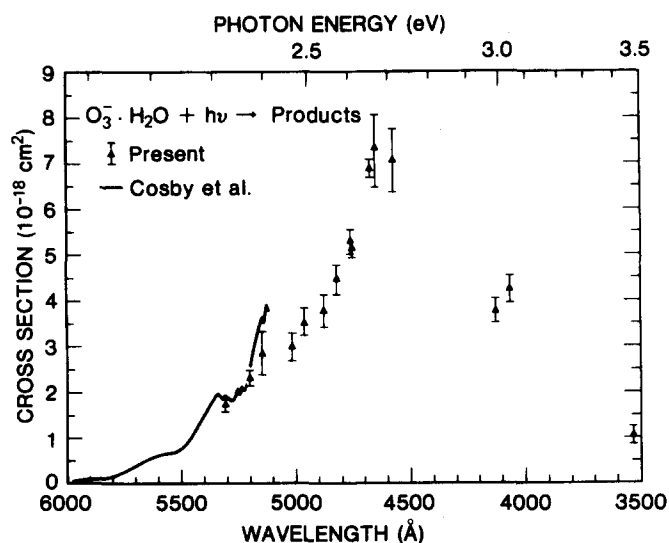The O_4^- ions may be photodestroyed by dissociative photodetachment

$$O_4^- + h\nu \rightarrow O_2 + e + O_2 \tag{15}$$

FIG. 7. The photodestruction cross section for $O_3^- \cdot H_2O$ in the 3500-6000 Å region. The measurements of Cosby *et al*. (Ref. 4) are indicated.

or by photodissociation

$$O_4^- + h\nu \rightarrow O_2^- + O_2 \; . \tag{16}$$

The photodestruction cross sections of O_4^- are shown in Fig. 8. The cross section at the UV line (66% 3507 Å and 34% 3569 Å) is $(8.64 \pm 0.80) \times 10^{-18}$ cm^2, which is not included in Fig. 8. The previous measurements given by Cosby *et al*.[2,3] and Smith *et al*.[5] are also shown. The photodestruction cross sections increase with increasing photon energy. The dependence of the O_4^- photodestruction cross section on wavelength is very similar to that of the O_2^- photodetachment cross section. This may suggest that the photodetachment process (15) is the dominant process for the photodestruction of O_4^-. The threshold for (15) is higher than the electron affinity for O_2 (0.440 eV)[34] by the O_4^- dissociation energy of 0.6 eV.[49] This threshold of 1.04 eV is consistent with the observed

threshold at ~9000 Å obtained by extrapolation of the cross section to zero. The rate of increase of the cross section changes at wavelengths of ~7500 and 5500 Å. This may be attributable to dissociative photodetachment of O_4^- into the excited states of O_2, in a manner similar to that observed in O_2^- photodetachment.

Burt[50] has reported that the average photodetachment cross section of O_4^- in the 4500 Å region is 9×10^{-18} cm^2. This value is larger than the present measurements by a factor of about four. However, Burt's measurements[50] contained a large experimental uncertainty.

G. OH⁻ and OD⁻

The OH⁻ ions are produced in a gas mixture of 2% CH$_4$ in O_2 by the reaction[51]

$$O^- + CH_4 \rightarrow OH^- + CH_3 \tag{17}$$

with a rate constant of 8×10^{-11} cm^3 sec^{-1}. With such a fast reaction rate, the O⁻ ions produced in the source region will be converted into OH⁻ within 1 cm when the CH$_4$ pressure is 4 mTorr and $E/N = 10$ Td. For a drift distance of 20 cm and an O_2 pressure of 0.2 Torr, the OH⁻ ions will experience about 1000 collisions before interacting with the laser; hence, the OH⁻ ions should be well relaxed and equilibrated with the surrounding gas at 300 K.

The OD⁻ ions are produced in a gas mixture of 2% CH$_4$ and 2% D$_2$ in O_2. The reaction of O⁻ and D$_2$ has two product channels,[52]

$$O^- + D_2 \rightarrow D_2O + e \tag{18}$$

$$\rightarrow OD^- + D \tag{19}$$

with rate constants of 4×10^{-10} and 1.5×10^{-11} cm^3 sec^{-1}, respectively. The rate for reaction (19) is very slow when compared with reactions (17) and (18). Therefore, OD⁻ is not primarily produced by reaction (19), but probably by the exchange process,
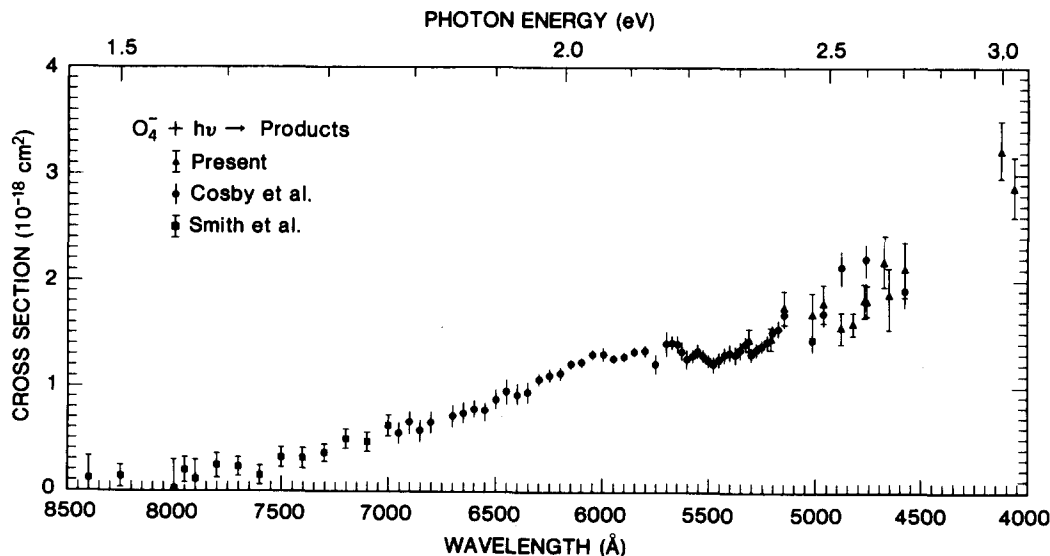
$$OH^- + D_2 \rightarrow OD^- + HD \; , \tag{20}$$

FIG. 8. The photodestruction cross section for O_4^- in the 4000–8500 Å region. The measurements of Cosby *et al*. (Refs. 2 and 3) and Smith *et al*. (Ref. 5) are shown.
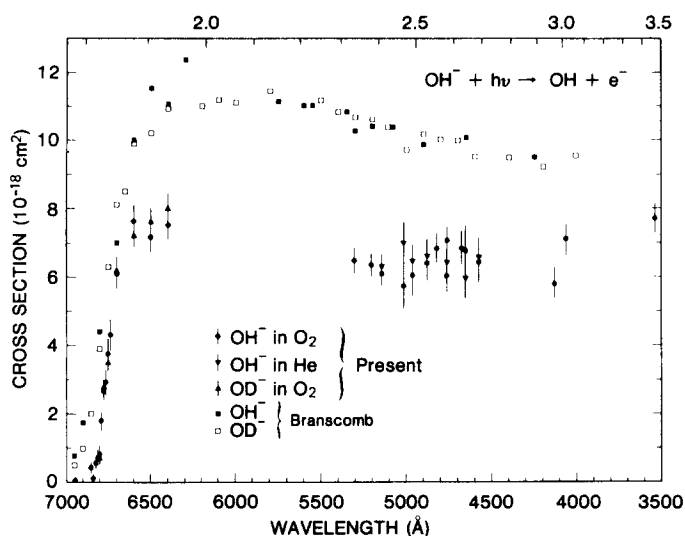
FIG. 9. The photodetachment cross sections for OH$^-$ and OD$^-$ in the 3500–700 Å region, measured in O_2 and He. The results of Branscomb (Ref. 18) are indicated for comparison.

where OH$^-$ is initially produced by reaction (17).

The photodestruction of OH$^-$ in the present photon energy region (<3.5 eV) occurs only through photodetachment,

$$OH^- + h\nu \rightarrow OH + e \ . \tag{21}$$

With electron affinities of 1.825 and 1.462 eV for OH[15] and O,[32] respectively, and a dissociation energy of 4.35 eV for OH,[53] the dissociation energy of OH$^-$ is 4.71 eV, which is higher than the photon energy region investigated here.

The mobilities of OH$^-$ and OD$^-$ in O_2 have not been measured. However, if mass scaling is used, their mobilities should be nearly equal to that of O$^-$ in O_2. This assumption was verified by measuring the cross sections of OH$^-$ in a gas mixture of 1% CH_4 and 2% O_2 in He. The mobilities of OH$^-$ and O$^-$ in He are known and are nearly equal.[23] The photodetachment cross sections of OH$^-$ and OD$^-$ measured both in O_2 and in He are shown in Fig. 9. Since the cross sections measured in both O_2 and He gases are consistent, the mobilities used for OH$^-$ and OD$^-$ in O_2 must be close to the real values.

The photodetachment cross sections of OH$^-$ and OD$^-$ have also been measured by Branscomb[18] and Warneck[19] using crossed ion and photon beams. Their measurements are consistent with each other, but are 40% higher than the present measurements. The data given by Branscomb[18] are also shown in Fig. 9 for comparison. The discrepancy may be partly inherent in the different experimental techniques. In Branscomb's experiment, the ions were produced in discharge with a high degree of internal excitation, in contrast to the present experiment where the ions are in thermal equilibrium at 300 K. Also, Branscomb's data represent average values over a photon bandwidth of 50 Å, in contrast to the narrow laser bandwidth (0.5 Å for dye lasers and less than 0.1 Å for the Ar$^+$ and Kr$^+$ ion lasers). Such technical differences may explain the discrepancy at the threshold,

where the cross section of Branscomb et al.[18] extends to slightly longer wavelengths than the present threshold. However, for wavelengths shorter than the threshold, both experimental techniques should give the same result. The cross section is not expected to be significantly affected by the bandwidth, because the cross section is nearly constant. It should not be affected by the rotational excitation, because the transition moments are not expected to be significantly different for the different rotational levels. Vibrational excitation may exist in the fast ion beam, although the vibrational spacing is high $[\omega_e = 3735$ cm^{-1} for OH$^-(^1\Sigma^+)]$.[18] However, considering the similarity between the potential curves for OH and OH$^-$, the photodetachment cross section is not expected to be significantly affected by the vibrational excitation. The discrepancy between these OH$^-$ measurements is large, when compared with the good agreement for the measurements of O^{-14} and O$_2^-$.[13] The possible experimental errors in the present measurements have been examined by measuring the cross section using various gas mixtures, gas pressures, and applied electric fields, but the results do not vary. At present, the discrepancy is not understood.

At the threshold, the present measurements agree quite well with the relative cross section measurements of Hotop et al.[15] The cross section shown in Fig. 9 has a sharp onset at 6795 ±5 Å (14713 ±11 cm^{-1}), in good agreement with the onset at 14 700 cm^{-1} observed by Hotop et al.[15] The sharp onset corresponds to the opening of the Q branches in the OH($X\,^2\Pi_{3/2}$) – OH$^-$($X\,^1\Sigma^+$) transition[15] and should have the same wavelength in both measurements. The OH$^-$ rotational temperature in the measurements of Hotop et al.[15] is about 1200 K, which is much higher than the temperature in the present measurements at 300 K. This results in the measurements of Hotop et al.[15] having a significant cross section at the wavelengths longer than the sharp onset, in contrast to the present measurements where the cross section at the longer wavelengths is small.

IV. CONCLUDING REMARKS

The photodestruction cross sections for O$^-$, O$_2^-$, O$_2^- \cdot H_2O$, O$_3^-$, O$_3^- \cdot H_2O$, O$_4^-$, OH$^-$, and OD$^-$ were measured in the 3500–5400 Å and 6300–8600 Å regions. The present results are generally consistent with other measurements, except for OH$^-$ and OD$^-$. For these two ions, the present results are about 40% lower than the measurements of Branscomb[18] and Warneck.[19]

The photodetachment cross sections at the thresholds for O$^-$ and OH$^-$ were investigated. The threshold wavelengths are in excellent agreement with other measurements.[15,32] The cross section near the O$^-$ threshold is well described by a threshold law. On the other hand, the increase in the photodetachment cross section for O$_2^-$ with increasing photon energy is attributed to the increase in accessible O_2 states, in contrast to the interpretation of Burch et al.[13] that the increase is explained by the threshold law.

Structure has been observed in the photodestruction cross section for O$_3^-$. This structure is attributed to the same progression previously observed at longer wave-

lengths. Detailed investigation of this structure is in progress.

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