two levels $a^2H_{11/2}$ and $b^4G_{11/2}$ given in AEL should be made, as indicated by the $g$ value observed for one of them, even though the observed and calculated separations of the two levels are large and agree well (i.e., 2758 $cm^{-1}$ and 2842 $cm^{-1}$, respectively). Our qualitative criteria for admitting the possibility of a critical dependence on the parameter values in this instance, are that the pure $LS$ levels are nearly degenerate, as can be seen from the left-hand column in Table VII, and there is no direct interaction between the pure levels to stabilize the composition.[16]

[16] This critical dependence of eigenvectors on the parameters is illustrated for a third-order matrix with a single parameter by E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1951), p. 39.

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# Photodetachment of $O_2^-$†

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The cross section for photodetachment of $O_2^-$ has been measured for the range of photon energies 0.5 to 3.0 ev. No onset energy is discovered in this range but analysis of the data gives an extrapolated threshold at $0.15\pm0.05$ ev. The curve is found to rise gradually with increasing slope, reaching a value of $2.4\times10^{-18}$ $cm^2$ at 3.0 ev photon energy. Comparison of the data with the predictions of threshold law theory and the results of previous experiments results in an interpretation in terms of assumed potential curves for $O_2^-$.

## I. INTRODUCTION

A GLANCE at the history of molecular-negative-ion research reveals a great many experiments which have been performed giving valuable information on their rates of production and destruction as well as their behavior under various circumstances. Most of these experiments have been necessarily of the swarm type involving mixtures of electrons, atoms, molecules, and ions with various distributions of energy. Unfortunately, the observations have seldom been unequivocally interpretable in terms of the microscopic character of the ions. The weakness of the forces which maintain negative ions causes them to be very delicate, which fact mitigates against their assembly in sufficiently high densities to permit spectroscopic research of the conventional types. Further, molecular ions have complicated structures, and this has hampered theoretical investigation of their nature. Thus, the mechanics of formation, the energy of binding, and the energy-level schemes have still not been established for any molecular negative ion.

Many different kinds of diatomic negative ions are now known to exist and among the most diligently studied of these has been the ion of oxygen, $O_2^-$. It is readily formed in gas discharges containing oxygen. The presence of small amounts of the gas in devices such as counters tubes can seriously affect their behavior by capture of electrons from the ionized plasma.[1] Also, the possibility that $O_2^-$ may form in the $D$ region of the ionosphere makes it of interest to several fields of study.[2]

The configuration of electrons in the ground state of $O_2^-$ is believed to consist of the orbitals of $O_2$ plus an extra electron in the antibonding $(\pi_g 2p)$ orbital.[3,4] Formation of the ion may take place by direct radiative attachment although the cross section for this process is expected to be very much smaller than is required to explain the copious production observed in gas discharges. Bloch and Bradbury[5] proposed that the electron capture leaves the ion in an excited vibrational level which is then stabilized by collision. This explanation also requires a cross section for the stabilizing collision considerably larger than is supposed likely.[6] It has also been suggested[7] that the ions may be formed in electron- or ion-exchange collisions of $O_2$ with $O^-$.

Published values of the binding energy of the extra electron of $O_2^-$ range from 0.07 ev[5] to 0.9 ev.[8] The low binding energy allows the ion to be destroyed easily by collisional detachment in discharges at high $E/p$.[9] It is also possible[7] that they may be destroyed in discharges by charge exchange in collisions with other types of molecules. Further, they may be destroyed by the

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[1] B. B. Rossi and H. H. Staub, *Ionization Chambers and Counters* (McGraw-Hill Book Company, Inc., New York, 1949), first edition, p. 29 ff.
[2] Smith, Burch, and Branscomb, Ann. Géophys. **14**, 225 (1958).
[3] H. S. W. Massey, *Negative Ions* (Cambridge University Press, Cambridge, 1950), second edition, p. 28.
[4] D. R. Bates and H. S. W. Massey, Trans. Roy. Soc. (London) **A239**, 269 (1943).
[5] F. Bloch and N. B. Bradbury, Phys. Rev. **48**, 689 (1935).
[6] H. S. W. Massey, reference 3, p. 72 ff.
[7] D. S. Burch and R. Geballe, Phys. Rev. **106**, 183 (1957); **106**, 188 (1957).
[8] I. A. Kazarnovski, Doklady Akad. Nauk S.S.S.R. **59**, 67 (1948).
[9] L. B. Loeb, Phys. Rev. **48**, 684 (1935).

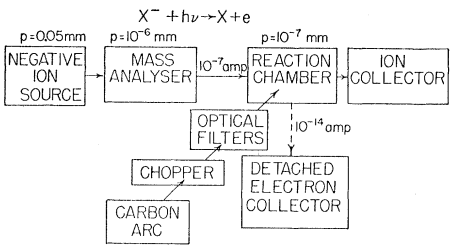


FIG. 1. Block diagram showing principle components of the equipment for a photodetachment experiment.

process of photodetachment, which is the subject of this paper.

The interaction of a photon and a negative molecular ion may result in absorption of the photon and excitation of the ion, or, if the photon energy is sufficiently large, it may be used to free the extra electron leaving a neutral molecule. In the case of $O_2^-$, photons in the infrared range of wavelengths have enough energy to cause photodetachment. This paper describes an experiment in which the cross section for the photodetachment process was measured for a range of photon energies from 0.5 to 3.0 ev.

## II. THE EXPERIMENT

### A. Method and Procedure

The details of the method and equipment of the experiment have been described in other papers[10,11] and it will suffice here to review these topics briefly, pointing out the items peculiar to the measurements on $O_2^-$. Figure 1 schematically depicts the essential components of the apparatus. Ions from a suitable source are accelerated in an electric field and dispersed magnetically so that ions of only one $e/m$ enter a high-vacuum reaction chamber where they must pass through a beam of light. The photodetachment reaction occurs at this intersection and the detached electrons are collected by weak electric and magnetic fields. Quantities measured include $j_e$, the photodetached electron current; $j_i$, the ion beam current; and $W$, the radiant power in the light beam. These quantities may be related,[10] for monochromatic light, by the proportionality

$$P = j_e/j_i \propto \sigma W \lambda, \qquad (1)$$

wherein $P$ is defined to be the experimental probability of photodetachment, $\lambda$ is the wavelength of the radiation, and $\sigma$ is the cross section. This relation may be used to obtain relative values of $\sigma$ for various wavelengths when the other quantities have been measured and parameters such as ion velocity are held constant during a run. The optical system we have used in this work is such that direct measurement of the absolute magnitude of $\sigma$ is not practicable. Experimental comparison, at one wavelength, of $P/W$ for $O_2^-$ with $P/W$ for another species of ion whose cross section is known absolutely at that wavelength, serves to put the relative measurements on an absolute scale.

In practice, we approximate the condition of monochromaticity of the radiation by inserting combinations of interference and absorption filters chosen to transmit only in a narrow band of wavelengths. The band passes of the filters are about 0.2 ev of photon energy which is approximately the spacing of vibrational levels in the ground electronic state of $O_2$ and, perhaps, of $O_2^-$. Therefore, the experiment cannot resolve the vibration-rotation structure.

As is the case in any spectroscopy, the possibility of a complete analysis of the data depends on a knowledge of the distribution in energy states of the sample under investigation. In this experiment, the sample ions are made under complex circumstances and must then be transported to the reaction chamber. While the formation mechanism will leave the ions in some distribution, this may become altered while the ions are making their way out of the source and to the light beam. However, neither the formation mechanism, nor even the exact circumstances obtaining in the regions where formation occurs are known. In lieu of such knowledge, we may possibly obtain pertinent information by (a) study of the ion source, and (b) experimental attempts to change the initial distribution. The discussion of the ion source and its operation in the following paragraphs has been written with attention to these considerations.

The ion source is the negative canal ray from a glow discharge source operated in oxygen at a pressure of about 25 microns Hg. Use of retarding potentials shows that the ions have a kinetic energy of approximately 300 ev with a spread of 25 ev at the exit of the anode aperture. The energy may be supplied from the space-charge potentials in the body of the discharge, from the potential on an electrode (called the repeller) which lies in the plasma near the anode, or a combination of these. At energies of from 25 to 300 ev, the sum of the collisional detachment and charge-exchange cross sections for $O_2^-$ is given by Hasted and Smith[12] to be $6\times10^{-16}$ cm$^2$. Thus, at 25$\mu$ Hg pressure, the mean free path for destruction of an ion will be of the order of 0.05 cm, which is about one-fifth of the length of the anode aperture. For $O_2$ in $O_2$ the collision mean free path at this pressure is about one centimeter while the probability per collision of loss of vibrational energy is $10^{-5}$ at room temperature.[13] These figures will be somewhat different for the case of $O_2^-$ in $O_2$ with ion energies of $\sim$100 ev, but the changes are not likely to exceed one or two orders of magnitude.[14] Thus, the mean free path for

[10] Branscomb, Burch, Smith, and Geltman, Phys. Rev. **111**, 504 (1958).
[11] S. J. Smith (to be published).
[12] J. H. Hasted and R. A. Smith, Proc. Roy. Soc. (London) **A235**, 349 (1956).
[13] L. S. Sinness and W. E. Roseveare, J. Chem. Phys. **4**, 427 (1936).
[14] This argument neglects transfer of vibrational energy of $O_2^-$ to the vibration-rotation system of $O_2$.

relaxation of vibrational energy of $O_2^-$ should be much greater than that for ion destruction.

The discharge path, which has a length of about 10 cm, is run with a potential difference of the order of one thousand volts. The positive column of the discharge is striated and the potential drop in the column is expected to be distributed at the striae heads[15] in steps of the order of one hundred volts over a distance of about one mean free path. The potential fall in the stria is inferred from the occasional presence in the mass spectrum of a secondary peak of $O_2^-$ ions with $\sim 100-200$ ev more energy than that of the ions in the main peak. A negative ion approaching a stria head will be accelerated to this energy and then will lose it again in collisions in the low-field regions between the striae. Since the fractional mean energy loss per elastic collision is of the order of one-half, the ions may have numerous collisions at energies sufficient for collisional detachment with high probability. These conjectures are strengthened by the observation that the source will not give a high yield of ions unless the discharge parameters are adjusted until a stria is very close to the anode. Thus, it seems probable that none of the ions can traverse the length of tube but, rather, that the processes of attachment and detachment take place alternately several times in the transit of a unit of charge.

The foregoing considerations imply that the ions approaching the anode are newly born and cannot have had their initial distribution in possible vibration-rotation energy states altered by collision. Accordingly, it seems reasonable that the distribution of those ions which pass through the anode to form the ion beam is determined mainly by the production mechanism. In addition, allowed optical transitions may take place during the 20 $\mu$sec of ion flight time from source to reaction chamber. On occasion, vapor of $D_2O$, which has a large dipole moment and is known to be very much more effective than pure $O_2$ in causing vibrational relaxation of $O_2$,[13] has been mixed with the $O_2$ in the discharge source but no differences in the $O_2^-$ photodetachment cross section were observed.

The ion-beam current is of the order of $5\times10^{-8}$ amp and the optical system permits approximately one-half watt of radiation to enter the reaction chamber. These values give rise to a current of $\sim 5\times10^{-14}$ amp of photodetached electrons. The filter combinations were used in a predetermined, cyclic order designed to reveal any systematic variation of experimental conditions during the run. Each combination was used three to five times. The resulting data were then applied to the calculation of relative values of cross section by the use of Eq. (1) and the results for each filter combination averaged.

[15] R. L. F. Boyd (private communication).

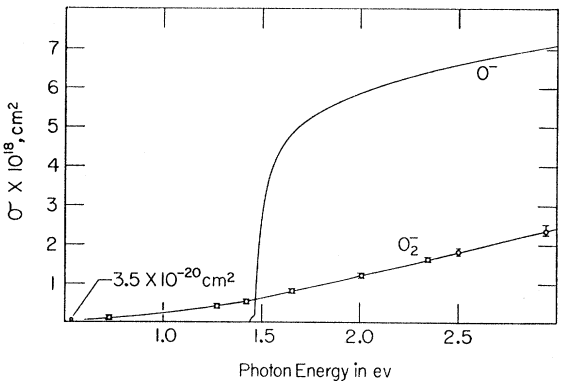


FIG. 2. Experimental photodetachment cross sections *vs* photon energy. The curve for $O^-$ is that given in a previous publication[10] and was used for normalization of the $O_2^-$ data. The solid curve drawn through the experimental points is a plot of Eq. (2) with the coefficients given in the text.

### B. Results

Relative values of cross section obtained by the procedure described above were made absolute by direct experimental comparison with the value for $O^-$ at 5400 A (2.38 ev). The comparison gave

$$\sigma(O_2^-)/\sigma(O^-)=0.25\pm0.01.$$

Since the value of $\sigma(O^-)$ at 5400 A is $(6.35\pm0.64)\times10^{-18}$ cm$^2$,[10] $\sigma(O_2^-)$ at this wavelength is therefore $(1.27\pm0.18)\times10^{-18}$ cm$^2$. The constant relating this value to our relative value of $\sigma(O_2^-)$ was then used to normalize the other relative values at the various wavelengths.

The results are shown in Fig. 2 in which the normalized values of $\sigma$ are plotted *vs* photon energy. The previously published curve for $O^-$ is also shown in Fig. 2 for comparison. Although the normalization procedure may introduce an error of $\pm14\%$ in the magnitude of the $O_2^-$ curve, the error bars, which indicate the average deviations of the sets of measurements made with each filter combination, define the shape of the full curve with considerably greater precision.

Geltman[16] has derived the energy dependence of the photodetachment cross section near threshold for diatomic negative ions. The data displayed in Fig. 2 can be fitted to his expression for a homonuclear ion having a $\sigma$, $\pi$, or $\delta$ outermost orbital with "gerade" symmetry. The threshold law for such an ion may be written

$$\sigma=E(E-E_0)^{\frac{1}{2}}[A_0+A_1(E-E_0)+A_2(E-E_0)^2+\cdots], \quad (2)$$

in which $E$ is the photon energy, $E_0$ is the energy at onset, and $A_0$, $A_1$, $A_2$, $\cdots$ are constants. At sufficiently small values of $(E-E_0)$, only the first term of Eq. (2) will be important. Denoting the experimental points by $S_i(E_i)$, a plot of $[E_i(E_i-E_0)^{\frac{1}{2}}/S_i]$ *vs*. $E_0$ for the smaller values of $E_i$ reveals the onset point to be $0.15\pm0.05$ ev. Using this value for $E_0$, a least-squares analysis of all

[16] S. Geltman, Phys. Rev. **112**, 176 (1958), following paper.

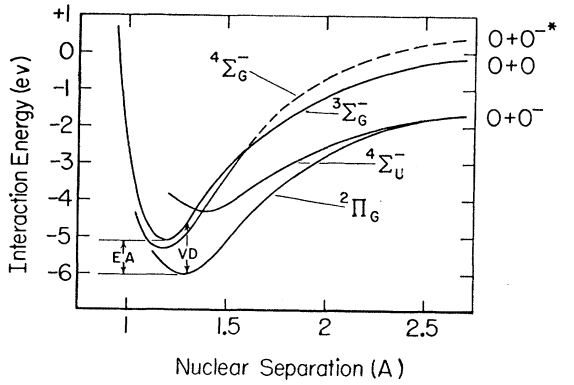


FIG. 3. Possible set of potential energy curves for $O_2^-$. The curve marked $^3\Sigma_g^-$ is for normal $O_2$.

the data indicates that only the first two terms of Eq. (2) need be considered for the energy range covered by the experiment. The analysis then gives

$$A_0=0.370\times10^{-17}\ \text{cm}^2\ \text{ev}^{-5/2},$$
$$A_1=0.071\times10^{-17}\ \text{cm}^2\ \text{ev}^{-7/2}.$$

The quality of the fit may be seen in Table I. The curve drawn through the points in Fig. 2 is a plot of Eq. (2) using the parameters obtained by the fitting procedure.

## III. DISCUSSION

Figure 3 represents a possible set of curves of potential energy *vs* internuclear separation for $O_2^-$ given by Bates and Massey[4] for illustrative purposes. The electron affinity shown is 0.9 ev, the value obtained by thermochemical studies, these being thought the most reliable,[17] and it is assumed that the ground state is $^2\Pi_g$. The curve marked $^3\Sigma_g^-$ for normal $O_2$ is of course, well known, as is the energy difference between the $^2\Pi_g(O_2^-)$ and $^3\Sigma_g^-(O_2)$ curves at infinite internuclear separation. This difference is equal to the electron affinity of atomic oxygen, 1.465 ev.[10] The curve marked $^4\Sigma_g^-$ is a state that would dissociate into O and $O^-$ if the latter were possible. Actually, it is believed that the excited state is not stable[18] and the ion will be subject to immediate auto-ionization at points above the intersection of the potential curve with that of $O_2$. The curve does not have any real significance in the region above the crossing points but is shown (dashed) in Fig. 3 to illustrate the considerations of this discussion. Below the crossing points, bound states can exist and the ion may be stabilized in the lower vibrational levels.

It is important to recall that even if all ions were in the ground electronic and vibrational state, if there is a difference in the equilibrium nuclear separations of $O_2$ and $O_2^-$, then the Franck-Condon principle would permit photodetachment to be operative only at photon energies equal to the vertical detachment energy (VD, Fig. 3) of $O_2^-$ rather than the electron affinity (EA) of $O_2$. If the ions are in some higher state, the threshold for detachment may lie at an energy less than the affinity. The vertical detachment energy for ground-state ions must be greater than or equal to the electron affinity for a molecule with positive affinity. The observation of photodetachment at photon energies as low as 0.54 ev implies then that either (a) $EA(O_2)<0.54$ ev or, (b) at least some of the ions are not in the ground state or, perhaps, both (a) and (b).

The form of Eq. (2) is appropriate to photodetachment to a single state of $O_2$ from a single vibrational level of the $^2\Pi_g$, $^4\Sigma_g^-$, or $^2\Pi_u$ electronic state of $O_2^-$. The $^2\Pi_u$ state is not shown in Fig. 3 but is believed[2] to have the minimum of its potential curve well above that for the ground state of $O_2$ and is not likely to be important to this discussion. In Sec. IIA, it was pointed out that the distribution in states of the ions used in the experiment is not likely to be altered by collisions. It is probable that the formation mechanism leaves the ions in only one electronic state although it may provide a distribution in vibrational levels.

In the process of fitting Eq. (2) to the data, an onset at $0.15\pm0.05$ ev was deduced. This is consistent with the value for the attachment energy of $0.13\pm0.06$ ev obtained by Bloch and Bradbury.[5,19] Further confirmation of the onset value is given by the experiments done by Loeb[9] which have shown that detachment of electrons from negative ions in a gaseous discharge of $O_2$ commences at a value of the ratio of field strength to pressure, $E/p\simeq90$ volts/cm mm. Varney[20] has measured the drift velocity, $v_d$, of $O_2^+$ in oxygen and Burch and Geballe[7] have concluded that the drift velocity of $O_2^-$ in $O_2$ is approximately equal to that of $O_2^+$. Varney's measured value of $v_d$ at $E/p=90$ v/cm mm is $1\times10^5$ cm/sec. From a formula given by Wannier,[21] the mean energy of an $O_2$ ion in an oxygen discharge is

$$E=\tfrac{3}{2}kT+mv_d^2.$$

At room temperature and with $v_d(O_2^-)=v_d(O_2^+)=10^5$ cm/sec, this relation gives a mean ion energy of 0.34 ev at the detachment threshold. Half of this energy may be used in an inelastic collision such as detachment, leading to an estimate of the detachment energy of again $\sim0.17$ ev.

No inferences concerning the shape or position of the potential curves of $O_2^-$ may be drawn from the value of the onset energy; since the vibrational level spacing of $O_2$ is $\sim0.2$ ev, the observation of an onset for detachment at 0.15 ev signifies only that in the experiments

[17] H. O. Pritchard, Chem. Revs. **52**, 529 (1953).
[18] L. M. Branscomb, *Advances in Electronics and Electron Physics* (Academic Press, Inc., New York, 1957), Vol. 9, p. 65.
[19] Recent findings of L. M. Chanin and M. A. Biondi (private communication) show a strong pressure dependence of the attachment coefficient at very low values of $E/p$ and may permit a revision of the Bloch-Bradbury theory of attachment of electrons to $O_2$.
[20] R. N. Varney, Phys. Rev. **89**, 708 (1953).
[21] G. Wannier, Bell System Tech. J. **32**, 170 (1953).

there is some nonempty vibrational level of $O_2^-$ which lies this much below some level of $O_2$ and that there is a region of overlap of the wave functions of the two states. Neither level need necessarily be the lowest in its electronic state.

That Eq. (2) fits the data so well over such a wide range of photon energy is rather surprising since in other studies of photodetachment[10] the first few terms of threshold laws have been found to be capable of fitting only that part of the cross-section curve between threshold and a few tenths of an electron volt above threshold. There are several ways in which the fit observed in this experiment may be accidental. It is possible that detachment is being observed from many vibrational levels of the $^4\Sigma_u^-$ state, whose threshold law rises as $E(E-E_0)^{\frac{1}{2}}$. Again, if the state from which detachment is occurring is $^2\Pi_g$ or $^4\Sigma_g^-$, with threshold shape $E(E-E_0)^{\frac{3}{2}}$, it may be that populations in various vibrational levels of $O_2^-$ and matrix elements for transitions from these to various levels of $O_2$ might combine in such a way that Eq. (2) is a good approximation to the total effect arising from all these transitions.

The simplest hypothesis which is in accord with *all* observations includes the following assumptions: (1) the photodetachment observed is a transition from a single level of $O_2^-(^2\Pi_g)$ or $O_2^-(^4\Sigma_g^-)$ to a single level of $O_2(^3\Sigma_g^-)$, i.e., Eq. (2) is the appropriate form of the threshold law; (2) the approximate form of the threshold law [Eq. (2)] is valid over the entire range of energy covered by the experiment; (3) the potential curves of these states lie approximately as pictured in Fig. 3. The last of these assumptions is required to preserve the value of affinity derived from thermochemical experiments.[8,22] The assumptions and observations of the photodetachment then imply that the reaction observed is probably

$$h\nu+O_2^-(^4\Sigma_g^-)\rightarrow e+O_2(^3\Sigma_g^-),$$

with $v''=0$ and $v'=0$. It is suggested that $O_2^-$ ions, when observed under gaseous discharge conditions, are stabilized in the $^4\Sigma_g^-$ state, which is very metastable with $^2\Pi_g$ since both states have gerade symmetry and the transition between them would be intercombinational. Inoue[23] has discussed the possibility of formation of the ions in the $^4\Sigma_g^-$ state. In thermochemical experiments involving $O_2^-$ in formation of crystals, interactions with neighboring ions may be sufficiently strong to cause the ions to enter the $^2\Pi_g$ state leading to observations of a value of $\sim$0.9 ev for the electron affinity of $O_2$. If the interpretations of such experiments should be erroneous and the $^2\Pi_g$ state lies higher than shown in Fig. 3, then there would be no need to consider the $^4\Sigma_g^-$ state in interpreting the photodetachment experiment, and the affinity inferred from these data and the swarm experiment would be about 0.15 ev.

TABLE I. For photons of energy $E_i$ given in the first column, the second and third columns give, respectively, the values of Eq. (2) (for the coefficients given in the text), and the experimentally determined values of photodetachment cross section.

| $E_i$ (ev) | $\sigma$ ($10^{-17}$ cm$^2$) | $S_i$ ($10^{-17}$ cm$^2$) |
|---|---|---|
| 0.531 | 0.043 | 0.035±0.009 |
| 0.728 | 0.105 | 0.094±0.019 |
| 1.278 | 0.446 | 0.427±0.065 |
| 1.419 | 0.569 | 0.575±0.036 |
| 1.653 | 0.807 | 0.823±0.050 |
| 2.009 | 1.215 | 1.23 ±0.04 |
| 2.348 | 1.646 | 1.62 ±0.03 |
| 2.938 | 2.370 | 2.39 ±0.15 |

[22] M. G. Evans and N. Uri, Trans. Faraday Soc. 45, 224 (1949).

[23] Yaji Inoue, Japan. J. Geophys. 1, 21 (1957).