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Dissociative attachment from the O_2 ($a^1\Delta_g$) state

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The dissociative attachment cross section for production of O^- by electron impact on the metastable $O_2(a^1\Delta_g)$ state is studied. The cross section is found to be $4.6 \pm 1.3 \times 10^{-18}$ cm^2 at its maximum. From the measured energy dependence, we infer that the dissociative attachment process takes place through the $O_2^-(^2\Pi_u)$ state as in the case of O^- production from the O_2 ground state. The information thus obtained is used to estimate the portion of the cross section for excitation of the $a^1\Delta_g$ state by electron impact which proceeds via the $O_2^-(^2\Pi_u)$ state. This mechanism is shown to account for the location and approximate magnitude of the maximum in the excitation cross section. Finally, information is obtained concerning the cross section for positive ionization of the $O_2(a^1\Delta_g)$ state near threshold.

I. INTRODUCTION

The dissociative attachment process in which negative ions are formed by electron impact is well understood for most common diatomic molecules in their ground states.[1] Dissociative attachment studies with molecules in excited states have thus far been restricted to those involving vibrationally and rotationally excited levels of the ground electronic state produced by thermal excitation.[2-4] The utility of these experiments is demonstrated by the empirical fitting by O'Malley[5] of the resonance dissociative attachment theory to the data of Henderson, Fite, and Brackmann[2] for negative ion production in hot O_2. In addition to reproducing the striking temperature dependence of the dissociative attachment cross section, O'Malley was able to deduce the repulsive portion of the potential curve of the O_2^- $(^2\Pi_u)$ state through which attachment takes place and estimate the autoionization lifetime of the repulsive state as a function of the internuclear separation.

The measurement of the dissociative attachment cross section from electronically excited molecules presents a considerable challenge experimentally because of the difficulties in combining monoenergetic electron beam techniques with the production of large densities of molecules in known electronically excited states. Molecular oxygen is an ideal system for an investigation of this kind because of the two low-lying metastable states, designated $a^1\Delta_g$ and $b^1\Sigma_g^+$, which are located 0.98 and 1.63 eV, respectively, above the ground state. The $a^1\Delta_g$ state, in particular, can be produced in suitable amounts because of its extreme stability against deactivation by collision with other molecules and with walls. Both metastable states and the $X^3\Sigma_g^-$ ground state are members of the ground electronic configuration of molecular oxygen and possess approximately the same internuclear separation and similarly shaped potential curves. For these reasons, the cross sections for production of O^- from the metastable states should resemble that from the ground state except in absolute magnitude and onset energy. No specific contribution to the production of O^- has been observed previously from these states although small amounts of electronically excited oxygen were undoubtedly produced in the oven sources used by other investigators.

The present paper describes an experiment in which the dissociative attachment process from the lower of the two metastable states of oxygen, the $a^1\Delta_g$ state, is studied. This reaction follows:

$$e + O_2(a^1\Delta_g) \rightarrow O^- + O. \tag{1}$$

Section II describes the apparatus and the technique used for production of molecules in the excited state. In Sec. III. A, the change in O^- production in the presence of the excited molecules is described. In Secs. III. B and III. C, a discussion is given of the means by which the concentration of molecules in the $a^1\Delta_g$ state is determined and the absolute magnitude of the dissociative attachment cross section is derived by normalization to the known cross section from the ground state. In III. D, a brief discussion is given of the positive ionization cross sections near threshold for the $a^1\Delta_g$ and $X^3\Sigma_g^-$ states.

Section IV interprets the experimental results in terms of the resonance theory of dissociative attachment. In particular, the knowledge of the dissociative attachment cross section from the excited $a^1\Delta_g$ state is used to derive information about the coupling between this state and the $O_2^-(^2\Pi_u)$ state. It is shown that the magnitude of the dissociative attachment cross section, together with the analysis of O'Malley, allow an estimate of the cross section for electron impact excitation of the $a^1\Delta_g$ state which proceeds through the intermediate O_2^- $(^2\Pi_u)$ ion. This mechanism follows:

$$e + O_2(X^3\Sigma_g^-) \rightarrow O_2^-(^2\Pi_u) \rightarrow O_2(a^1\Delta_g) + e. \tag{2}$$

The resonance contribution to the excitation cross

section is shown to be the dominant means of excitation at 7.8 eV.

To conclude this introduction, it should be noted that collision processes involving molecules in the $O_2(a^1\Delta_g)$ state occur in a great many interesting contexts which cannot be appropriately discussed here. Access to the literature may be made through several recent review papers.[6-8]

II. EXPERIMENT

A. Apparatus

The apparatus is shown schematically in Fig. 1. Oxygen flowing through 12-mm-o.d. Pyrex tubing is subjected to a 30–100 W microwave discharge at a frequency of 2450 MHz. The oxygen pressure in the region of the discharge is typically 0.1 torr. The discharged gas enters the main vacuum envelope by effusing from a slit in the end of the Pyrex tubing. The distance between the microwave cavity and the gas entrance slit is adjustable from 10 to 100 cm. A right angle bend in the Pyrex tubing serves to isolate the collision chamber from light produced in the discharge.

When long transit times are desired, the cavity is positioned about 50 cm from the gas entrance slit and the auxiliary roughing pump shown in Fig. 1 is not used. The discharged gas is therefore pumped only through the gas entrance slit. During the course of the experiment, several slits were used having lengths of 0.5 cm and widths ranging from 0.025 to 0.10 cm.

The stainless steel vacuum envelope is pumped by a 6 in. oil diffusion pump topped with a liquid N_2 cold trap. The background pressure in the system before bakeout is approximately 2×10^{-8} torr. Bakeout further reduces the background to 1×10^{-9} torr. Considerable care was taken to use good gas handling techniques. An analysis provided with the reagent grade oxygen indicated that the total N- and H-bearing impurities were less than 30 ppm.

Figure 2 shows in greater detail the geometry of the gas entrance slit and the electron beam collision chamber. To produce a high target density, the distance between the gas slit and the intersecting electron beam is quite short, about 1.5 cm. Because no additional collimation or differential pumping of the effusing gas is used following the slit, the high target density is paid for by a correspondingly high background pressure. However, with the geometry and pumping speed described here, the background density is at least a factor of 10 less than the density at the electron beam, a level which is easily tolerated in the present experiment.

B. Electron Beam

A magnetically collimated trochoidal monochromator is used to produce the electron beam. This

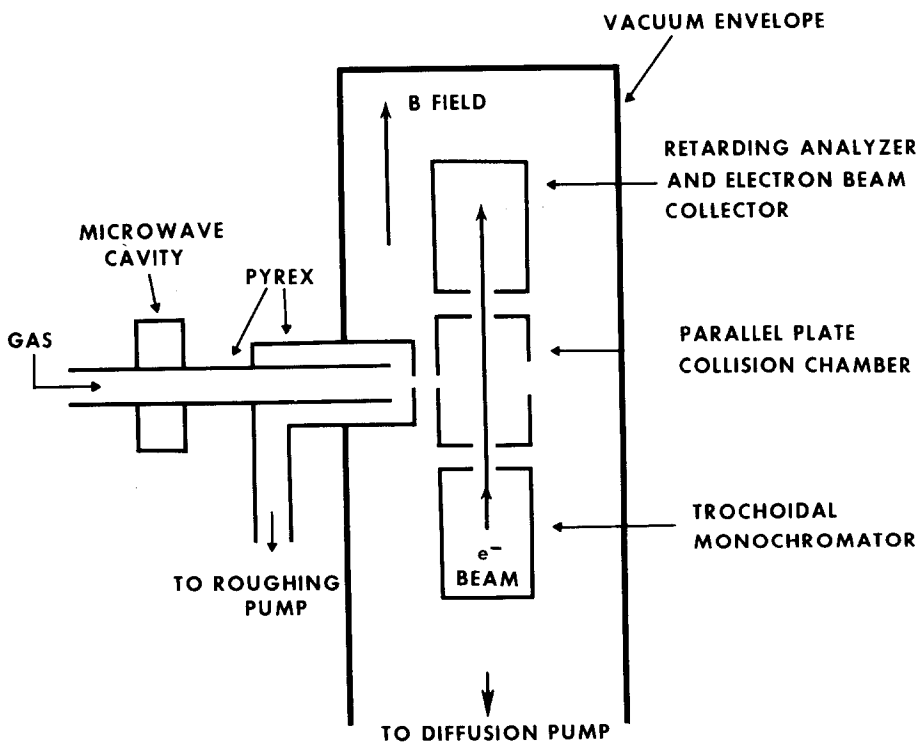

FIG. 1. Schematic diagram of the apparatus.

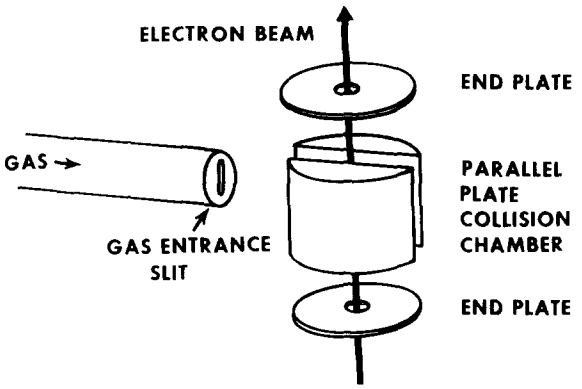

FIG. 2. Exploded view of the gas entrance slit and the parallel plate collision chamber. The slit and the electron beam are separated by about 1.5 cm.

type of monochromator has been previously described in detail by Stamatovic and Schulz[9] and used in several applications in which both magnetic collimation of the electron beam and high energy resolution were desired. In the present experiment, the monochromator was operated at beam currents in the 1×10^{-8} A range with a full width at half-maximum of 60–80 meV. An externally mounted pair of coils in the Helmholtz configuration provided a uniform magnetic field of 200–250 G for electron beam collimation.

An exploded view of the collision chamber is shown in Fig. 2. The two parallel plates which are used for current collection are spaced by 0.64 cm. Both of the endplates and the current collecting plates are positioned and electrically insulated from each other by small sapphire balls which are seated in carefully machined holes.

The remaining portion of the electron beam apparatus consists of a series of retarding plates for analysis of the electron energy distribution and a collection plate for the primary electron beam. All of the electrodes are made of a nonmagnetic copper–nickel alloy and are plated electrolytically with gold. A vibrating-reed electrometer is used for measurement of low currents.

C. Modes of Operation

By placing the appropriate bias voltages on the parallel collection plates with respect to the endplates, a number of modes of operation are possible. Ions of both signs can be collected either with both plates connected together or by using a single plate for current measurement and the opposite plate as an ion pusher by means of a transverse electric field.

With both parallel plates connected together and biased positively with respect to the endplates, the collision chamber operates in the trapped-electron mode.[10] In this method, an electrostatic well is created along the axis of the collision chamber. At electron impact energies just above the thresholds for inelastic processes, the resulting low-energy electrons are trapped in the well and migrate across the magnetic field lines to the collector plates by means of elastic collisions. The details of this technique have been discussed by Schulz.[10] In the present experiment, the trapped-electron method is used as an indicator of the relative number of molecules in the ground state with the discharge on and off. This application is discussed in greater detail in Sec. III.B.

D. Production of Excited Species

Microwave discharges in pure oxygen are well known to be useful sources for O_2 molecules in the $a^1\Delta_g$ state.[6–8] Depending on experimental conditions, electrodeless discharges may also produce a variety of other atomic and molecular species which are not desirable for the present experiment. For example, molecules in the upper metastable $b^1\Sigma_g^+$ state and vibrationally excited molecules in the ground electronic state yield O^- under electron impact which might be confused with that from the $a^1\Delta_g$ state. Dissociation may also take place in the discharge. Although atomic oxygen does not contribute to the O^- current under electron impact, its presence introduces an error in the procedure for measuring the density of molecules in the $a^1\Delta_g$ state as described in Sec. III.B. and it is therefore an undesired constituent. In this section we discuss briefly each of the species produced by microwave discharges in oxygen and the means by which all but the $a^1\Delta_g$ molecules may be largely suppressed.

1. Metastable $a^1\Delta_g$ Molecules

Downstream from a microwave discharge, molecules in the $a^1\Delta_g$ state occur in amounts estimated to be from 5% to 25%; a typical value would be 10%.[6] The rate constants for deactivation by collisions with most molecules are quite small. In particular, deactivation by ground state O_2 takes place with a rate constant[11] of $1.7\pm0.1\times10^{-18}$ cm^3 molecule^{-1} · sec^{-1}. Because the gas phase deactivation is so slow at pressures below 1 torr, destruction by wall collisions is the primary loss mechanism in most flow experiments in pure oxygen. The coefficient for destruction[12] on clean Pyrex, however, is only $1-2\times10^{-5}$. Because of this remarkable stability, molecules in the $a^1\Delta_g$ state may be pumped at slow speeds through rather large distances in substantial concentrations.

2. Metastable $b^1\Sigma_g^+$ Molecules

Molecules in the upper metastable state, $b^1\Sigma_g^+$,

are always observed to occur in smaller amounts than the $a^1\Delta_g$ state in flow experiments. Their deactivation rate[11] by collision with ground state molecular oxygen is 1.5×10^{-16} cm^3 molecule$^{-1}\cdot$sec^{-1}, a factor of 100 larger than that of the $a^1\Delta_g$ state. More significantly, deactivation by collision with Pyrex walls is also more probable[12] by a factor of 100. In an apparatus in which the concentration of $a^1\Delta_g$ molecules is intentionally reduced by long transit times and multiple wall collisions, these greater destruction rates make it unlikely that $b^1\Sigma_g^+$ molecules produced in or near the discharge region will survive.[13] Indeed, this species does not appear to have been detected by mass spectrometric methods.

3. *Vibrationally Excited Molecules*

Vibrationally excited molecules in the electronic ground state cause a dramatic increase in the O^- production by electron impact as studied by Henderson, Fite, and Brackmann.[2] In their experiment, the molecules effused directly from an oven source into a low-pressure collision-free region thus preserving the vibrational content. In flow experiments, however, the number of molecules in vibrationally excited states is quickly attenuated by the rapid vibration–vibration transfer rate which relaxes the higher states to the $v=1$ level. Ultimately the vibration–translation and wall deactivation processes relax the gas to its ground state. Appreciable amounts of molecules in excited vibrational levels, nitrogen in most studies, have been observed only in flow systems using very high-speed pumping.[14] At low pressures and long transit times following the discharge, the destruction of vibrationally excited molecules is primarily due to wall collisions. Although the wall destruction coefficients are not well known, there is no evidence that this species can survive in the amounts necessary to cause an error in the measured O^- current from the $a^1\Delta_g$ state.[15] An experimental test to substantiate this conclusion is discussed in Sec. III. D.

4. *Atomic Oxygen*

The production of atomic oxygen in its ^3P ground state is especially difficult to predict quantitatively because the amount of dissociation in the discharge is particularly sensitive to impurities, especially those bearing nitrogen and hydrogen. Generally, it is found that the higher the gas purity, the lower the percentage of atomic oxygen produced. Kaufman and Kelso[16] reported that for the purest gas they used, in a fast flow system, the dissociation was only 0.9%. At low pressures, the primary loss mechanism for the atomic oxygen produced in the discharge is recombination on the container walls. The coefficient for recombination[17] on Pyrex is 1.1×10^{-4}.

To summarize this section, all of the undesired species produced in the microwave discharge possess wall destruction coefficients which are at least a factor of 10 greater than that of the $a^1\Delta_g$ molecules. By using low pressures and sufficiently long transit times between the microwave source and the electron beam collision chamber, species other than $a^1\Delta_g$ molecules may be suppressed to a satisfactory level. The approach used in the present work is to attenuate the density of $a^1\Delta_g$ molecules below that attained with the shortest transit times and fastest flow speeds available in this apparatus. With the percentage of $a^1\Delta_g$ molecules reduced from 8%–10% to below 5%, the undesired species cause a negligible error.[18]

III. RESULTS

A. O^- Production by Dissociative Attachment

The relative cross section for production of O^- by electron impact on oxygen in its ground state is shown by the closed circles in Fig. 3 as measured with the microwave discharge off. The characteristic bell-shaped curve is in good agreement with previous investigators.[19,20] The energy scale was calibrated by using the known onsets for excitation of energy levels both in oxygen[21] and in an admixture of argon and oxygen by means of the trapped-electron method. The energy at which the maximum of the dissociative attachment cross section occurs, 6.7 eV, was in agreement with that found by Schulz.[19] The apparent energy at which O^- production begins was found to be sensitive to a number of factors such as the means used for extrapolation of the O^- current to zero, the high energy portion of the electron energy distribution, and the sensitivity with which the signal was being measured and, therefore, does not appear to be useful for calibration purposes.

The O^- production with the microwave discharge turned on is illustrated in the curve with open triangles in Fig. 3. A shift of the peak position to lower energy is apparent together with a considerably lower threshold for O^- production. Within experimental error, little change in O^- production was observed above 7.5 eV with the discharge on. Care was taken to ensure that the energy of the electron beam was not altered by shifting contact potentials after the discharge was turned on.

The O^- production as a function of electron impact energy with the microwave discharge on was measured under a number of experimental conditions including variations in the oxygen pressure in the discharge region, the transit time between discharge and electron beam, and microwave input power. In all cases, the essential features as described above were preserved, namely, enhanced

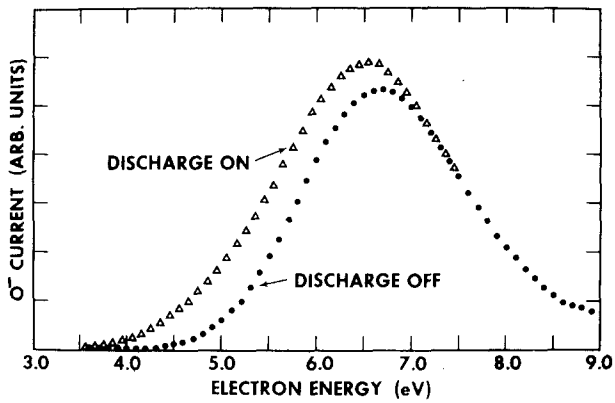

FIG. 3. The O^- current as a function of the electron impact energy with the microwave discharge on and off.

negative ion production in the electron energy range from 3.5 to 7.5 eV.[22]

B. Density of $a^1\Delta_g$ Molecules

To evaluate the cross section for dissociative attachment from the $a^1\Delta_g$ state from data such as those given in Fig. 3, it is necessary to know the density of molecules in the excited state. If no species other than molecules in the $a^1\Delta_g$ and $X^3\Sigma_g^-$ states enter the collision chamber, the trapped-electron method may be used to find the percentage of excited states by means of a "missing signal" technique.

The trapped-electron spectrum of ground state O_2 was first studied by Schulz and Dowell.[21] Using small well depths, 100 meV for example, the trapped-electron current as a function of electron impact energy consists of a series of peaks whose heights are proportional to the cross section for excitation to the various electronically excited states evaluated 100 meV above their thresholds. Of particular interest for the present application is a large, narrow peak near 10 eV. This peak, which is well isolated from other structures, remains sharp in trapped-electron spectra taken with even deeper wells. This indicates a cross section which is sharply peaked just above its threshold. Excitation of similar states in other gases, notably the $E^3\Sigma_g^+$ state of N_2, has been well studied.[23] Because the peak in the trapped-electron current is characteristic of a transition from the ground $X^3\Sigma_g^-$ state of O_2, its height is therefore proportional to the density of ground state molecules at the electron beam. With the microwave discharge turned on, the removal of molecules from the ground state, due to population of the $a^1\Delta_g$ state, results in a decrease in the magnitude of the trapped-electron current.[24] This procedure allows, therefore, a measurement of the ratio of the densities of $a^1\Delta_g$ molecules to $X^3\Sigma_g^-$ molecules. The importance of eliminating atomic oxygen from the gas entering the collision chamber is clear as this species would cause the ratio to be erroneously large.

Using this technique, the density of $a^1\Delta_g$ molecules surviving to the electron beam location was found to be approximately 3%–4% of the total gas density for the long transit times used here.

C. Dissociative Attachment Cross Section from the $a^1\Delta_g$ State

The change in O^- current with the discharge on and off, together with the appropriate allowance for the decrease in density of the ground state molecules with the discharge on, yield the contribution from the $a^1\Delta_g$ state. The dissociative attachment cross section may now be put on an absolute basis by referring the O^- current from the $a^1\Delta_g$ state to that from the ground state. For normalization we take the maximum in the dissociative attachment cross section from the ground state to be $1.3\pm0.2\times10^{-18}$ cm^2 as measured by Schulz.[19]

Figure 4 shows the energy dependence of the dissociative attachment cross section from the O_2 $(a^1\Delta_g)$ state. At its maximum, the cross section is $4.6\pm1.3\times10^{-18}$ cm^2, a factor of 3.5 ± 1 times larger than the maximum from the ground electronic state. As anticipated, the energy dependence of the cross section shown in Fig. 4 resembles that from the ground state shifted to lower energy by 0.98 eV, the separation between the $a^1\Delta_g$ and $X^3\Sigma_g^-$ states. A detailed discussion of the cross sections is given in Sec. IV. A.

D. Positive Ionization Cross Sections Near Threshold

The presence of $a^1\Delta_g$ molecules with the discharge on was also established by the appearance of positive ions below the threshold for ionization of the ground state. Detection of the excited molecule by traditional mass spectroscopy, first done by Foner and Hudson,[25] has not been widely used. Because the onset for O_2^+ production occurs only 0.98 eV below that for ionization from the ground state, good energy resolution is required in the ionizing electron beam. A more substantial problem inhibiting the usefulness of this technique is that the magnitude of the ionization cross section of the $a^1\Delta_g$ state is not known near threshold and thus absolute determination of excited state densities cannot be made.

Using the present apparatus, a measurement was made of the ratio of the positive ionization cross section for the $a^1\Delta_g$ state to the $X^3\Sigma_g^-$ state at approximately 0.5 eV above each respective threshold. The same technique for determination of excited state density was used as described in Sec. III. B.

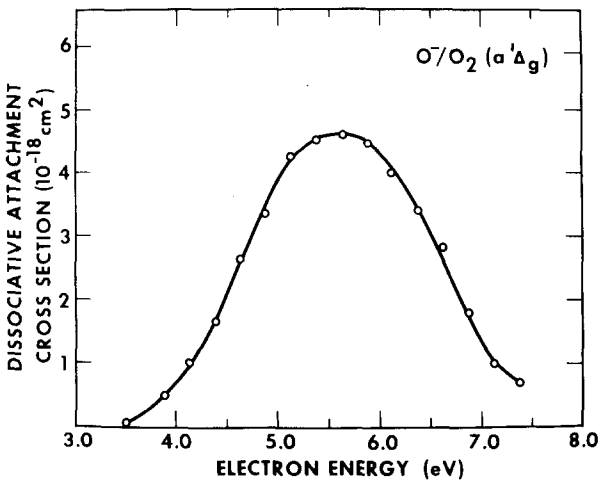

FIG. 4. The dissociative attachment cross section for production of O^- from $O_2(a^1\Delta_g)$ as a function of electron impact energy. The normalization is determined by reference to the dissociative attachment cross section from the ground state which is taken to be 1.3×10^{-18} cm^2 at maximum.

The ratio for $a^1\Delta_g$ to $X^3\Sigma_g^-$ was found to be 0.8 ± 0.3. Within the rather limited accuracy of this measurement, the ratio substantiates the assumption of equal positive ionization cross sections near threshold made by several previous investigators.[17,25]

As indicated earlier, the presence of vibrationally excited O_2 in the collision chamber would lead to enhanced O^- production under electron impact. With the experimental conditions which were used, the survival of vibrationally excited molecules is very unlikely. It is possible to verify that the enhanced O^- production does not arise from molecules in the first vibrational level of the electronic ground state, which are the most likely to survive. The production of positive ions at electron energies well below the threshold for ionization from the ground state can be unambiguously associated with the $a^1\Delta_g$ state rather than molecules with $v=1$. The ratio of O_2^+ current produced from the $a^1\Delta_g$ molecules to O^- current at electron impact energies below 4.3 eV would therefore be expected to remain constant under all experimental conditions if the same excited state were responsible for both currents. This ratio was measured with a number of parameters altered to change the density of $a^1\Delta_g$ molecules and was found to be constant within reasonable error.

IV. DISCUSSION

A. O^- Formation from the $X^3\Sigma_g^-$ and $a^1\Delta_g$ States

In the energy range from 4 to 9 eV, the production of O^- from the ground state of O_2 is understood to take place by the formation of an intermediate state of O_2^- designated $^2\Pi_u$. A simplified diagram showing potential energy as a function of internuclear separation is given in Fig. 5. This drawing includes only the $a^1\Delta_g$ and $X^3\Sigma_g^-$ states[26] and the $O_2^-(^2\Pi_u)$ state as derived by O'Malley's analysis.[5]

The dissociative attachment process can be qualitatively described, using the resonance model, as the product of two factors. The first of these is the cross section for formation of $O_2^-(^2\Pi_u)$ or capture cross section. The second factor is the survival probability,[27] that is, the probability that dissociation of the O_2^- molecule into $O+O^-$ will occur rather than autoionization. Quantitatively, the dissociative attachment cross section, except for a constant numerical factor, is given[27,28] by the expression,

$$Q \sim (g\Gamma_i f/k^2)\exp[-\int(\Gamma/\hbar)dt], \tag{3}$$

where k is the wavenumber of the incident electron, f is the overlap integral between the nuclear wavefunctions of the initial O_2 state and the intermediate O_2^- state, and g is the degeneracy factor determined from the spins of these same states.[29] The integration over time is performed from the time of formation of the O_2^- ion to the time of dissociation. The exponential factor is the survival probability which varies strongly with Γ, the total autoionization width of the intermediate O_2^- state.[30]

If autoionization takes place before dissociation the O_2 molecule may be left in one of its electronically or vibrationally excited states as well as in its ground state. The total autoionization width, Γ, is therefore equal to the sum of a number of partial widths, each of which is related to the probability that the decay process leaves the O_2 molecule in a

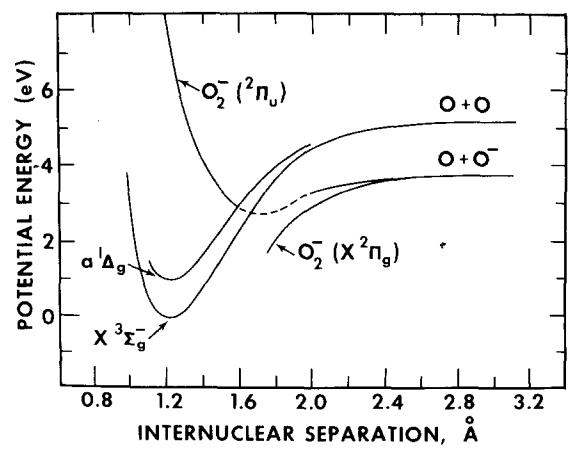

FIG. 5. Simplified diagram showing potential energy as a function of internuclear separation (from Ref. 5).

given final state. The term Γ_t in the pre-exponential factor, that is, the capture cross section, is the partial width for decay back to the initial O_2 state. This width is identical to the partial width for entry into the O_2^- state from the initial O_2 state and is a measure of the strength of the transition between the two states.

By fitting the resonance dissociative attachment theory to the temperature dependence of the O^- production from the ground electronic state as measured by Henderson *et al.*,[2] O'Malley[5] was able to derive both the potential energy curve and the total autoionization width of the $O_2^-(^2\Pi_u)$ state. The partial width for decay back to the ground state was determined by normalizing the theoretical expression to the dissociative attachment cross section measured by Schulz.[19]

The expression for the dissociative attachment cross section, as given above, indicates that the cross section is completely determined by the potential energy curves of the initial O_2 and intermediate O_2^- states and the autoionization width of the latter. It is well known that the spectral constants for the $a^1\Delta_g$ and $X^3\Sigma_g^-$ states are very similar: The internuclear separations[31] differ by only 0.008 Å and the Franck–Condon factor[32] for the ground vibrational levels is 0.9869. The dissociative attachment cross sections from these two states, therefore, are expected to be very similar except for a numerical factor due to the difference in spin factor, entry width, and electron energy at which the process takes place. All of these factors are contained in the expression for the capture cross section.

A detailed comparison of the shapes of the dissociative attachment cross sections is made in Fig. 6. In this drawing, the cross section from the $a^1\Delta_g$ state has been shifted to higher energy by 0.98 eV, the spacing between the $a^1\Delta_g$ and $X^3\Sigma_g^-$ states, and the magnitude has been normalized to the cross section from the ground state for ease of comparison. In addition to the shift to higher energy, the dissociative attachment cross section from the $a^1\Delta_g$ state has been multiplied by $(E-0.98)/E$ where E is the electron energy in electron volts. This removes the slight difference in shape due to the k^{-2} dependence of the capture cross section which results from the smaller separation between the $a^1\Delta_g$ and $O_2^-(^2\Pi_u)$ states. The striking similarity of the two cross sections confirms our expectation that O^- production from the $a^1\Delta_g$ state also proceeds through the same intermediate formation of $O_2^-(^2\Pi_u)$.

By utilizing the resonance theory of dissociative attachment further, we can gain more understanding of the coupling between the $O_2^-(^2\Pi_u)$ state and the members of the O_2 ground state configuration. In Sec. III.C., the dissociative attachment cross section from the $a^1\Delta_g$ state was found to be 3.5 ± 1 times that from the ground state at their respective maxima. Because the survival probability is essentially the same for dissociative attachment initiated from either the $a^1\Delta_g$ or $X^3\Sigma_g^-$ state, we can write

$$g_a\Gamma_a/k_a^2 \simeq (3.5\pm1)g_x\Gamma_x/k_x^2, \tag{4}$$

where the subscripts a and x refer to the $a^1\Delta_g$ and $X^3\Sigma_g^-$ states, respectively. Using the known spin factors $g_a=2$ and $g_x=\frac{2}{3}$, and the electron energies at which the maxima in the respective cross sections occur, we solve for the partial decay width from $O_2^-(^2\Pi_u)$ into the $a^1\Delta_g$ state in terms of that into the $X^3\Sigma_g^-$ state, obtaining

$$\Gamma_a = (1\pm0.3)\Gamma_x. \tag{5}$$

That is, the $O_2^-(^2\Pi_u)$ intermediate state, when formed by electron impact on the ground state, decays in approximately equal amounts into the ground vibrational level of the $a^1\Delta_g$ and $X^3\Sigma_g^-$ states. In view of the symmetry of these two transitions with respect to changes in spin and angular momentum, this result seems very plausible.

B. Excitation of the $a^1\Delta_g$ State by Electron Impact

The excitation cross section of the $a^1\Delta_g$ state is of considerable interest at low electron energy because the transition from the ground state is forbidden by electric dipole selection rules. The direct excitation by electron impact is expected to be small except near threshold where exchange effects might dominate. A modified Born approximation calculation of the cross section, including exchange, was first carried out by Watson *et al.*[33] using semiempirical parameters. Their cross section reached its maximum value of 6×10^{-19} cm^2 at 1 eV above the threshold for excitation. The experimentally determined cross section, measured by Trajmar, Cartwright, and Williams,[32] is considerably larger, reaching a magnitude of almost 1×10^{-17} cm^2 at its peak near 7 eV. A more recent calculation using the Ochkur–Rudge approximation for the exchange amplitude has been carried out by Julienne and Krauss[34] and is in much better agreement with the experimental data. Above an electron impact energy of 15 eV, the theoretical cross section falls within the experimental error bars. Below this energy the cross section, which is maximum near 11 eV, considerably underestimates the experimental value. To account for the excitation at low energies, both in magnitude and in location of the maximum, it is necessary to examine indirect or resonant processes which may contribute to the cross section.

As a byproduct of the dissociative attachment

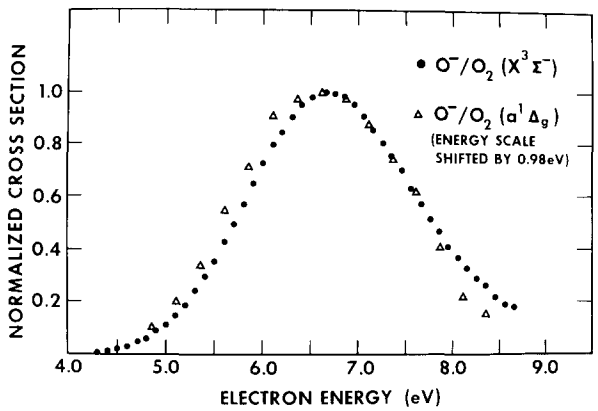

FIG. 6. The normalized cross sections for dissociative attachment from $O_2(a^1\Delta_g)$ and $O_2(X^3\Sigma_g^-)$ states as a function of electron impact energy. The $a^1\Delta_g$ cross section has been shifted to higher energy by 0.98 eV and modified as described in the text.

measurement reported here, it is possible to estimate the contribution of the $O_2^-(^2\Pi_u)$ state to the cross section for electron impact excitation of the $a^1\Delta_g$ state from the ground state. This reaction follows:

$$e + O_2(X^3\Sigma_g^-) \rightarrow O_2^-(^2\Pi_u) \rightarrow O_2(a^1\Delta_g) + e. \qquad (2)$$

O'Malley[5] was the first to indicate that this mechanism could contribute to the excitation of the $a^1\Delta_g$ state.[35] At that time the partial decay rates of the negative ion were unknown and the size of the contribution could not be determined.

The portion of the cross section for excitation of the $a^1\Delta_g$ state proceeding through the $O_2^-(^2\Pi_u)$ state is estimated in the following way. According to O'Malley,[5] the capture cross section for entry into the $O_2^-(^2\Pi_u)$ state from the ground state has its maximum value of about 1×10^{-16} cm^2 at an energy of 7.8 eV. O'Malley states that at least half of the compound state decays into the high-lying $A^3\Sigma_u^+$ and $C^3\Delta_u$ states, not shown in Fig. 5, which lead to neutral dissociation. Of the remainder, about half goes to the ground vibrational level of the $X^3\Sigma_g^-$ ground state. The discussion in Sec. IV.A of the present paper implies that the other half goes predominantly to the ground vibrational level of the $a^1\Delta_g$ state. This yields a cross section for excitation of the $a^1\Delta_g$ state of approximately 2.5×10^{-17} cm^2 at an energy of 7.8 eV. It is important to emphasize that this estimate is rather crude. The accuracy of the branching ratios was not specified by O'Malley. However, the cross section deduced here would appear to be an upper bound on the true value.

The total cross section measured by Trajmar *et al.*[32] is shown by the closed circles in Fig. 7. Although their data points are too widely spaced to locate the maximum in the cross section more closely, the largest measured values, 9.1×10^{-18} cm^2 ±24%, occurs at 7.0 eV. Near this energy it appears that the excitation proceeding through the $O_2^-(^2\Pi_u)$ state estimated above is sufficiently large to account for the entire cross section observed experimentally.

A more detailed comparison of the energy dependence for excitation to the $a^1\Delta_g$ state can be made in order to illustrate the range over which the mechanism discussed here is important. The portion of the excitation which proceeds through the $O_2^-(^2\Pi_u)$ state should reflect to good approximation the energy dependence of the capture cross section derived by O'Malley. This is shown by the solid line in Fig. 7, normalized to the experimental data at 7.0 eV for convenience of comparison. The maximum in the excitation cross section would therefore be expected to lie at 7.8 eV. This feature has been substantiated in a measurement of the electron excitation of the $a^1\Delta_g$ state by Wong, Boness, and Schulz[36] who located the maximum at 8.0±0.3 eV.

A substantial amount of excitation to the $a^1\Delta_g$ state takes place both above and below the energy range of the $O_2^-(^2\Pi_u)$ capture cross section. Although the present dissociative attachment study does not yield information on this additional excita-

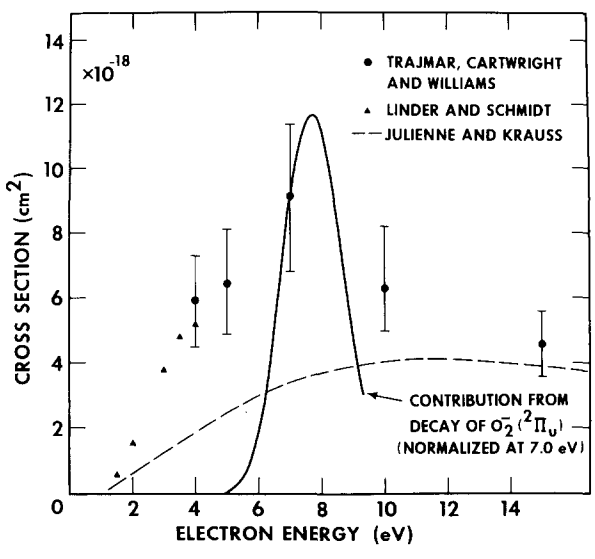

FIG. 7. The total cross section for electron excitation of the $O_2(a^1\Delta_g)$ state as a function of electron energy. The solid line shows the contribution from the decay of the $O_2^-(^2\Pi_u)$ state normalized to the experimental data of Trajmar *et al.* at 7 eV. The dashed line shows the Ochkur–Rudge calculation of Julienne and Krauss.

tion, it is tempting to speculate that at least a portion of the excitation arises from the decay of other repulsive O_2^- states. Above an impact energy of 8 eV, this interpretation would appear to be quite routine. Recent calculations[37,38] have located many O_2^- states which intersect the Franck–Condon region of the ground state at higher energies. In addition to excitation of the $a^1\Delta_g$ state by means of autoionization, these states should also cause the production of O^- in this energy range. This view is supported by the dissociative attachment data[19,20,39] which show a small, relatively constant, yield of O^- from 10 to 17 eV. The fraction of the total cross section which is due to resonance processes cannot be easily extracted. However, the exchange cross section calculated by Julienne and Krauss[34] would be expected to under-estimate the total cross section in the energy range 6–15 eV. Figure 7 shows this to be the case.

The excitation of the $a^1\Delta_g$ state which occurs below the onset of the $O_2^-(^2\Pi_u)$ capture cross section is not as easily interpreted. Linder and Schmidt,[40] whose data are also shown as the filled triangles in Fig. 7, have studied the excitation process from 1.5 to 4 eV and confirm the magnitude of the cross section. None of the calculated O_2^- states appear to intersect the Franck–Condon region of the ground state of O_2 at substantially lower energies than the $^2\Pi_u$ state.[38] However, the calculations yield only the real part of the potential curves. If autoionization is strong in the Franck–Condon region of the ground state, the curves will be considerably broadened and excitation could take place at lower energies. Wong *et al.*[36] have observed strong excitation of the vibrational levels of the O_2 ground state which they interpret as proceeding predominantly through the $^2\Sigma_u^-$ and $^4\Sigma_u^-$ states of O_2^- and possibly other states as well. Their cross sections for vibrational excitation peak near 9 eV and have an onset between 3.5 and 4 eV. In contrast to this behavior, the cross section for excitation of the $a^1\Delta_g$ state, as seen in Fig. 7, is still relatively large below 4 eV. This energy dependence appears to rule out any excitation proceeding through the $O_2^-(^2\Sigma_u^-$ and $^2\Sigma_g^+)$ states.[41] The most likely means of excitation of the $a^1\Delta_g$ state from threshold to 5 eV therefore appears to be nonresonant exchange scattering. Although the calculation of Julienne and Krauss[34] underestimates the measured cross section in this region, the Ochkur–Rudge approximation is inaccurate at low energies because of the neglect of the distortion of the incident electron wavefunction and the polarization of the molecule.

V. CONCLUSIONS

This work has shown that the production of O^- from the $O_2(a^1\Delta_g)$ state by electron impact takes place through the intermediate formation of the $O_2^-(^2\Pi_u)$ state. The dissociative attachment cross section at its maximum was found to be 3.5 ± 1 times larger than that for the ground state. This implies that the $O_2^-(^2\Pi_u)$ state decays by autoionization into the ground vibrational levels of the $O_2(X^3\Sigma_g^-)$ and $O_2(a^1\Delta_g)$ states in approximately equal amounts. It should be noted that these two decay channels and the channels mentioned earlier, namely the $A^3\Sigma_u^+$ and $C^3\Delta_u$ states, appear to account for most of the decay of the $O_2^-(^2\Pi_u)$ state. This implies that excitation near 7.8 eV to the metastable $b^1\Sigma_g^+$ state and to higher vibrational levels of the $a^1\Delta_g$ and $X^3\Sigma_g^-$ states must be considerably smaller than that to the ground vibrational level of the $a^1\Delta_g$ state. This conclusion is verified in part by the measurements of Trajmar *et al.*[32] who found the cross section for excitation to the $b^1\Sigma_g^+$ state to be 4.5 times smaller than that of the $a^1\Delta_g$ state.

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