Dissociative Attachment of Electrons to Hot Oxygen*

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Crossed beam experiments on dissociative attachment to form O^- ions in collisions of electrons with oxygen molecules are described. In these experiments the temperature of the oxygen beam source was varied and very strong changes in the cross section as a function of temperature were displayed indicating marked enhancement of the cross section with increasing internal energy in the O_2 prior to the collision with the electron. A separate thermal equilibrium experiment verified the accepted affinity of ground state O^-, and experiments using free jet expansion of the heated O_2 indicated that the form of internal energy responsible for the enhancement of the cross section is vibrational excitation, in accord with the theory given by T. F. O'Malley. Absolute determinations of the cross sections at different temperatures were made and found to be in accord with O'Malley's predictions.

I. INTRODUCTION

In dissociative attachment of electrons to molecular oxygen

$$e + O_2 \rightarrow O + O^-$$
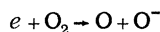
conservation of energy requires that the electron energy E is given by

$$E = \mathfrak{D} - A + (KE)_O + (KE)_{O^-} ,$$

where $\mathfrak{D}$ is the dissociation energy of the neutral molecule, A is the electron affinity of the O^- negative ions, and the (KE) are the kinetic energies of the dissociating O and O^-. Since the kinetic energies of the products can never be negative, a minimum electron energy, equal to $\mathfrak{D} - A$, is required for dissociative attachment to proceed. For oxygen, for which $\mathfrak{D} = 5.08$ eV and $A = 1.465$ eV,[1] one would not expect O^- to be formed in electron collisions with molecules at electron energies less than about 3.6 eV.

This energy consideration played an important role in an experiment of two of us (WLF and RTB) about six years ago which attempted to study radiative attachment of electrons to free oxygen atoms.[2] The experiment was one in which a modulated neutral beam containing oxygen atoms was to be crossed by an electron beam and O^- was to be detected mass spectrometrically. Since gas discharge and thermal dissociation sources for beams of oxygen atoms do not fully dissociate the gas, molecular oxygen would be present in the beams, and it was important to avoid production of O^- ions formed by dissociative attachment to the molecules. This was presumed straightforward to do by merely limiting the electron energies in the experiment to less

than 3.6 eV.

The experiment was first tried using a gas-discharge source for the atomic oxygen. It was found that large O^- signals appeared at electron energies down to 1 eV and less. There was no doubt, however, that these signals were associated with molecules rather than atoms in the neutral beam on the basis of the phase at which the signals appeared in the modulated beam experiment, the phase being related to the time of flight, and therefore the mass, of the neutrals in the beam.[2] It seemed clear that the process being observed was dissociative attachment to molecules that had been internally excited in the gas discharge and for which the dissociation energy had been reduced to less than the ground-state value.

To exclude contributions to O^- signal from excited molecules, the gas-discharge oxygen-beam source was replaced by a thermal dissociation furnace source operating at about 2000°K. Again the experiment was attempted, but again large O^- signals were seen at electron energies well below 3.6 eV, and again phase information of the modulated signals unequivocally associated these ions with oxygen molecules rather than atoms. Evidently those molecules which were excited thermally were responsible.

Since with the 2000°K furnace source the population of internally excited states is described by a Boltzmann distribution, only about one in 400 molecules could have as much as 1-eV internal energy; at the same time, the strength of the signals at electron energies of 1 eV below the accepted threshold for O^- production from O_2 in the ground state were quite comparable with the maximum signal that could be obtained when the oxygen beam was not heated. It was clear that internal energy of the order of 1 eV per degree

of freedom in the oxygen increased the dissociative attachment cross section for reasons unknown by about two orders of magnitude!

These preliminary experimental results were reported in 1963. Shortly thereafter Yu. N. Demkov[3] argued qualitatively that vibrational excitation could be the form of internal energy that led to enhancement of the cross section. Demkov noted that the dissociative attachment process involves the formation of a transient $(O_2^-)^*$ ion which either auto-ionizes back to $e + O_2$ or dissociates into $O + O^-$, and that the relative probability of the latter process will increase rapidly with internuclear separation at the instant of attachment to form the $(O_2^-)^*$. Since the maximum internuclear separation will increase with vibrational excitation, Demkov concluded that vibrational excitation will lead to increased O^- production.

The experiments were continued at the University of Pittsburgh, and a second interim report in 1965[4] included a limited amount of data on O^- signal as a function of O_2 temperature. T. F. O'Malley[5] used these data along with the basic model of Demkov and constructed a quantitative theory of the phenomenon, which included the deduction of the principal features of the state of $(O_2^-)^*$, which upon dissociation produces the O^-.

The present paper summarizes the final experimental situation. Credence is given to O'Malley's theory through the verification of absolute cross-section magnitudes which were not available when the theory was formulated. Additionally the paper presents direct experimental evidence that vibrational excitation is necessary for the cross-section enhancement, and lastly the results of an experimental measurement of the affinity of O^- using thermal equilibrium methods giving agreement with the value from photodetachment measurements.[1]

II. EXPERIMENTAL METHODS AND RESULTS

The apparatus used in these studies was a two-stage differentially pumped molecular beam machine. The experimental arrangement was as shown in Fig. 1.

The first chamber housed the hot-oxygen beam source, which was a 2 in. length of welded iridium tubing of o.d. $\frac{1}{4}$ in. and wall thickness of 0.020 in. The iridium tubing was silver soldered into stainless-steel end pieces which in turn were fitted to the water-cooled arms of the furnace mount. Oxygen gas flowed down a channel in one of the mounting arms and was admitted at one end of the furnace. Pressure inside the furnace was measured at the opposite end in order to minimize problems in pressure determination due to flow
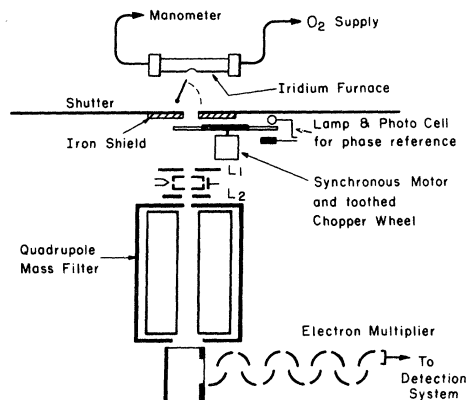

FIG. 1. Schematic of the crossed beam experiment to study dissociative attachment of electrons to heated oxygen gas.

effects. At about the midpoint along the length of the furnace, a small aperture allowed the gas which would form the molecular beam to emerge. Iridium foil baffles were placed inside the furnace to ensure better uniformity of temperature in the volume near the aperture and also to give more surface area for collisions of the gas with the walls. The average number of wall collisions per molecule before emerging in the molecular beam was estimated to be 1000 or more. The temperature of the furnace was measured using an optical pyrometer looking through a quartz window down one end of the furnace and viewing the inside furnace wall adjacent to the exit aperture. A photo-electric pyrometer working in the infrared was used to monitor and stabilize the furnace temperature during measurements.

Electric current carried by the water-cooled mounting arms heated the furnace resistively, and a variable autotransformer and transformer in series were used to provide the 3 V at approximately 300 A needed to heat the furnace to its maximum temperature of 2100°K. Normally the furnace was biased positively with respect to the grounded vacuum-chamber walls in order to prevent thermionic electrons from escaping, traveling along with the molecular beam and providing false signals through collisions with the background gas in the second chamber.

An aperture in the wall separating the two vacuum chambers collimated the oxygen beam. On entering the second, or experimental, chamber, the neutral beam was modulated at slightly less than 1440 cps by a toothed wheel driven by a synchronous motor operating from an audio oscillator and power amplifier. A metal plate with an aperture L_1 gave final collimation to the neutral beam and also served to shield out any electrostatic fields produced in the area of the

chopper wheel.

An equipotential shield surrounded the region of interaction between the neutral and the electron beams. The electrons were produced by a tungsten filament, were confined by a longitudinal magnetic field, and were collected by a tungsten surface which was heated to dull red. Heating of the collector was adopted after experiments indicated that electron reflection is reduced at such a surface, leading to more accurate measurements of the electron current and minimizing signal contributions from reflected electrons. Unwanted modulated magnetic fields in the interaction region were excluded by using high-permeability shielding between the furnace and the interaction region.

The equipotential shield around the interaction region was made from gold-plated copper and was operated at approximately 200°C to minimize buildup of surface contaminants, the charging of which could cause potential shifts.

Ions produced in the interaction region were removed axially, i.e., parallel to the direction of the original neutral beam. Under these circumstances the initial momentum of the neutral particle from which the ion is formed tends to carry the ion out. Additional ion extraction was provided by the weak field from the ion lens, L_2, which penetrated back through the neutral-beam exit aperture in the interaction region shield. L_1 was as the same potential as the interaction region shield to minimize fields penetrating into the interaction region from the neutral-beam entrance end.

After leaving L_2, the ions entered a quadrupole mass filter which transmitted only ions of a given e/m ratio. The ion energy during traversal of the mass filter was typically 30 to 50 eV. Upon emergence from the mass filter the ions were detected by being drawn through a large aperture in the side of a cylindrical tube, which was placed on axis at the exit of the mass filter. The ions were drawn through the aperture by the field from the high voltage on the first dynode of a 14-stage Cu-Be electron multiplier. This arrangement excluded the possibility of noise arising from photoelectric effect, which would have been intolerable had the first dynode of the multiplier been exposed directly to light from the furnace and the electron gun.

Signal current at the anode was capacitively coupled to a preamplifier and phase-detection system. Output from the detector was recorded by a balancing pen recorder. Phase reference for the detector came from a lamp and photocell unit monitoring the motion of the toothed wheel that modulated the neutral beam. Ion currents of the order of 10^{-18}A could be measured in this arrangement.

The absolute electron energy was determined by assigning the value 6.7 eV to the energy at which the peak of the curve for dissociative attachment

to room-temperature O_2 occurs, this value having been previously determined by Craggs and Tozer[6] and by Schulz.[7] Absolute cross-section values were assigned by normalizing the peak of the relative cross-section curve for dissociative attachment to room-temperature oxygen to the value obtained by Schulz, namely, 1.25×10^{-18} cm^2.

A comparison of the room-temperature oxygen cross sections in the present experiment and in that of Schulz[7] is shown in Fig. 2. This comparison is instructive for two reasons. First, the close similarity of shape is to be noted. In the Schulz experiment all ions were collected irrespective of their kinetic energy on formation and his curve should be a true total cross section.
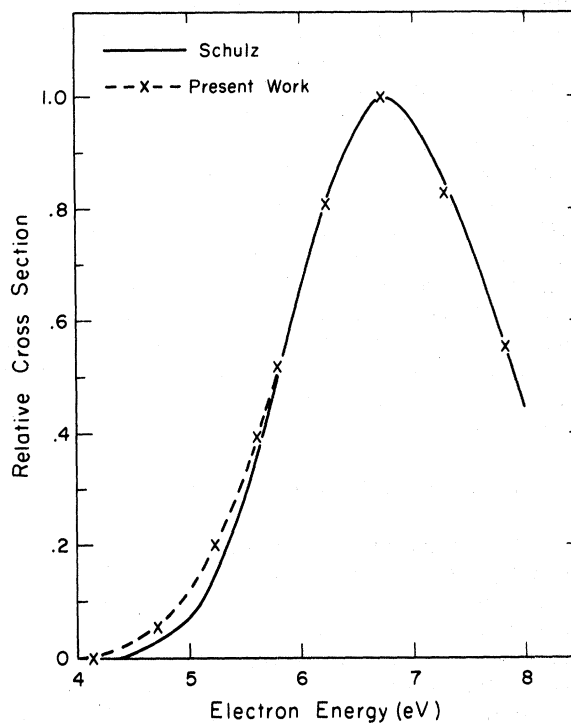

FIG. 2. Comparison of the total cross-section curve of Schulz (Ref. 7) for dissociative attachment of electrons to room-temperature oxygen and that obtained in the present experiments.

In the present experiment an unknown fraction of the total ions formed was focussed into the mass filter and were ultimately detected. Since the energy of the ions on formation depends on the electron energy [see Eq. (1)], the shapes of the two curves should be different if the ion-collection efficiency in the present experiment were strongly dependent on the initial ion energy. The fact that the shapes are very similar argues that the ion-collection efficiency in the present experiment is not strongly energy-dependent, and that signals obtained should be directly proportional to total

cross sections to good approximation.

The second point to notice is that the crosses (present experiment) in Fig. 2 lie very slightly higher than the results of Schulz at the lowest-electron energies. This is to be expected since Schulz used the retarding potential difference method, and his effective energy spread was smaller than the thermal energy spread from the tungsten-filament gun used in the present experiment.

In order to determine absolute cross sections when the furnace temperature was changed, the signals per unit current were multiplied by $(T/300)^{1/2}$ where T was the absolute temperature. This correction, which accounts for a change of number density in the oxygen beam as the furnace temperature affects the molecular speeds, is appropriate if (1) the total gas flow in the beam is constant, (2) the furnace operates in the free molecular flow regime, and (3) the ion-detection efficiency is independent of the speed of the molecule from which the ion is formed.[8] The first two conditions were readily met experimentally.

The apparent independence of ion-collection efficiency noted above in connection with Fig. 2 argues that the third condition was met as well, since the range of contribution to ion velocities due to changes of speed of the molecules from which the ions are formed is very much less than the range of ion velocities encountered in dissociative attachment to room-temperature O_2 as the electron energy is changed.

III. RESULTS ON DISSOCIATIVE ATTACHMENT

Figure 3 graphically displays the effect that heating the O_2 produces on the cross section for the production of O^-. It is similar to the data presented in Ref. 4 except that in the data shown there O^- signals were given, whereas in Fig. 3 correction has been made for molecular velocity to yield cross-sectional information. The most striking feature of the results is that the appearance potential is shifted by about 2.5 eV upon raising the temperature of the oxygen to only about $\frac{1}{6}$ eV.

Assurance that the effect shown in Fig. 3 is physical rather than instrumental was directly obtained by substituting CO, NO, and NO_2 and finding no such shift occurring in the O^- production. D^- production from D_2 was examined, but signal-to-noise problems were very severe in this case because of the small dissociative attachment cross section. It could only be determined that no gross shift, as in the case of O_2, was present. There would seem no doubt that the shift and enhancement of the dissociative attachment curve with internal energy is not characteristic of all dissociative attachment reactions. (Note that P. J. Chantry[9] has recently studied N_2O and finds even more
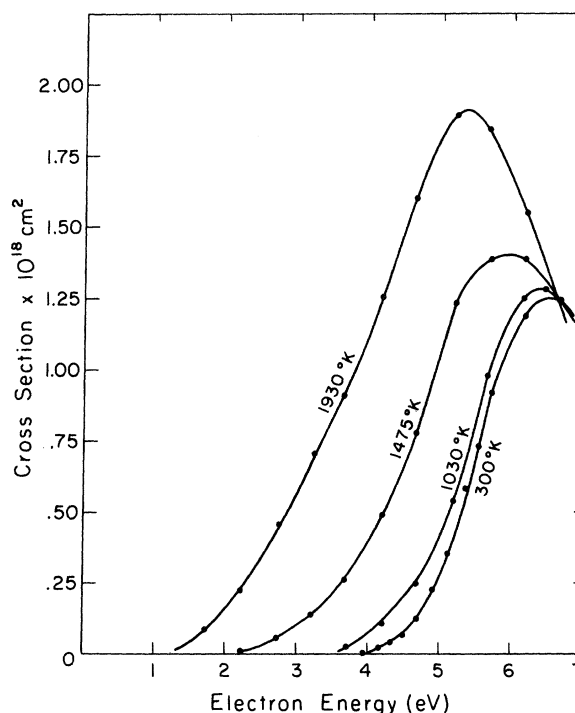
FIG. 3. Total cross sections for dissociative attachment of electrons to O_2 as a function of temperature of the O_2. Absolute values have been assigned taking Schulz's (Ref. 7) value of 1.25×10^{-18} cm^2 at the peak of the cross section for room temperature O_2.

striking temperature effects in dissociative attachment than appear in O_2.)

Considering the question of energy, Eq. (2) requires that the electron energy $E \geq \mathfrak{D} - A$. Since ions are observed at energies down to 1.5 eV and since the affinity, $A = 1.465$ eV, the molecules from which the ions observed were produced at the lowest-electron energies must have had dissociation energies $\mathfrak{D} < 3.0$ eV. Since the ground-state dissociation energy is 5.08 eV, evidently these molecules had internal energies of at least 2.1 eV.

As noted in the introduction to this paper, the appearance of observable signals implies that the cross sections for dissociative attachment to such highly excited molecules must be quite enormous by virtue of the fact that in the thermal equilibrium case exceedingly few molecules are so highly excited.

Given this qualitative conclusion, it was appropriate to examine the type of internal excitation that could lead to such a strong enhancement of signal. The fact that the O_2 molecule has two electronic states, the $a^1\Delta_g$ and the $b^1\Sigma_g^+$, lying respectively at 1.0 and 1.6 eV above the ground state suggested that these might be involved. In order to investigate this possibility, studies of

the O^- production at fixed electron energy as a function of the oxygen furnace temperature were performed. Since the Boltzmann population of either of these two excited states should be as $\exp(-E_i/kT)$ where E_i represents the energy of either of these electronic states, the signals of O^- ions from these states should depend on temperature in the same way. If only one of these states were responsible the data should, when plotted on a graph of log signal versus $1/T$, give the well-known straight-line Arrhenius plot with the energy of the responsible state playing the roles of the chemists' activation energy. Should more than one state enter, the graph would consist of breaking straight-line segments with an over-all curvature that is concave upward. It was anticipated that any discrete state(s) responsible should be identifiable from their energies as displayed in the slopes of the line segments on such graphs.

Data obtained when varying the oxygen temperature while holding the electron energy fixed are shown in Fig. 4. To within the accuracy of the data, the curves on a plot of log signal versus $1/T$ appear to be straight lines over the entire temperature range accessible to the experiment for electron energies below the threshold for producing O^- from cold O_2. Correcting the O^- signal data shown in Fig. 4 by $(T/300)^{1/2}$ to account for change in number density in the beam with furnace temperature change gives absolute cross-section curves on an Arrhenius plot which are again indistinguishable from straight lines. From these results and results of the type shown in Fig. 3, it appears that the effective cross section $Q(E, T)$ as a function of electron energy E, and oxygen temperature T, is well described by

$$Q(E, T) = C(E) \exp[-D(E)/kT], \tag{3}$$

where

$$C(E) = 2 \times 10^{-13}(0.06E^2 + 0.012E$$

$$- 0.14) \exp(-2.09E) \quad (\text{cm}^2) \,,$$

with E being given in eV, over the range of E from 2 to 5 eV. Values of $D(E)$ are shown in Fig. 5, which suggests that $D(E)$ may be a linearly decreasing function of E over the range of the measurements.

Since the excitation energy of the lowest electronically excited state of $O_2(a^1\Delta_g)$ is 1.0 eV and since values of $D(E)$ of less than 1.0 eV appear, it seems that electronic excitation cannot be the cause of the phenomena shown in Figs. 3 and 4. Further, as best as can be judged, $D(E)$ does not seem to be quantized over the energy range of measurement (2 to 5 eV). Although not
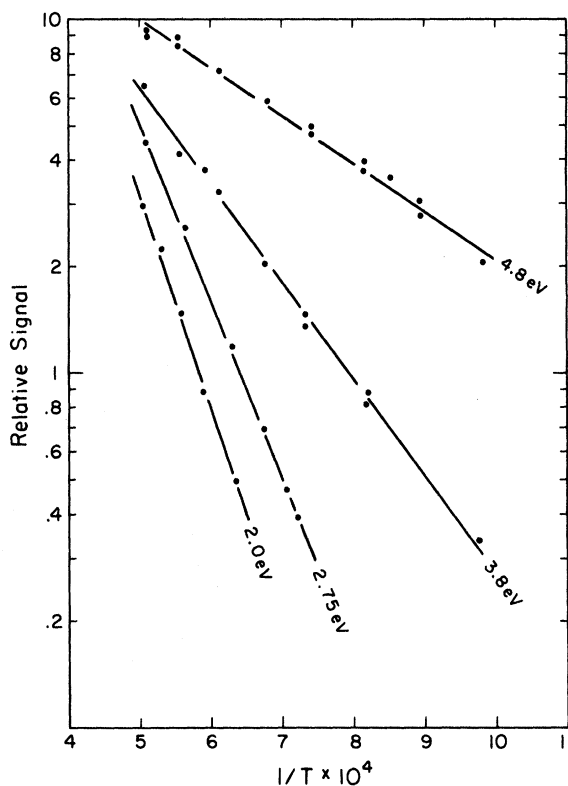

FIG. 4. Plots of O^- signals versus $1/T$ as a function of electron energy displaying the electron-energy–dependent activation energy $D(E)$.

evident from Fig. 5, experiments in which values of $D(E)$ were determined at two slightly different electron energies during a given day's running suggest that $D(E)$ is continuously variable.

To interpret the experimental finding, Eq. (3), it must be recognized that the effective cross section, $Q(E, T)$ is the average of the separate cross sections for each internal energy state, averaged over the distribution of internal energy states of the O_2. Since this distribution is that for thermal equilibrium,

$$Q(E, T) = \frac{\sum_j \sigma_j(E) w_j \exp(-u_j/kT)}{\sum_j w_j \exp(-u_j/kT)} \,, \tag{4}$$

where u_j is the energy and w_j is the statistical weight of the jth state of O_2 and $\sigma_j(E)$ is the electron-energy–dependent cross section for dissociative attachment for this state.

In general, one would not expect $Q(E, T)$ to be of the form of Eq. (3) where $D(E)$ is not quantized. However, where energy levels are sufficiently closely spaced, this situation does obtain. For example, if rotational excitation alone were re-
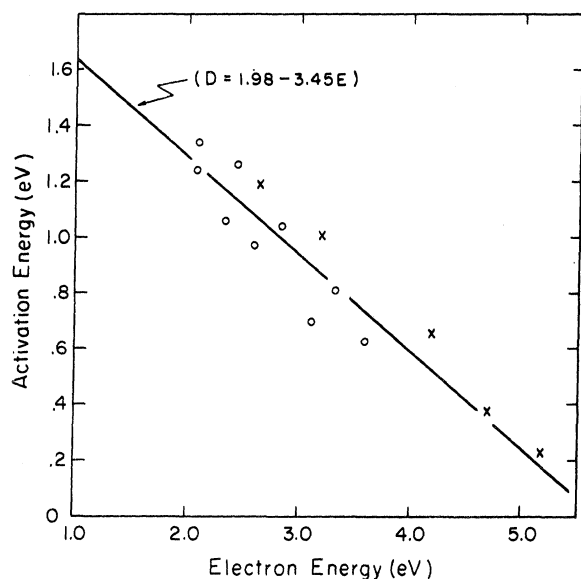
FIG. 5. Plot of the activation energy, $D(E)$ versus electron energy in dissociative attachment of electrons to oxygen molecules.

sponsible for the observations, we would have $u_j = Bj(j+1)\hbar^2$ and $w_j = 2j + 1$; since the energy spacing between states of successive j is very much smaller than the values of j appropriate to the high temperatures of the experiment, a continuous description can replace the sum in Eq. (4) with negligible error. In this approximation for rotational excitation alone,

$$Q(E, T) = (1/kT) \int_0^\infty \sigma(u, E) \exp(-u/kT) du, \quad (5)$$

where u is the internal energy. The most obvious form for $\sigma(u, E)$ which upon substitution gives Eq. (3) is

$$\sigma(u, E) = \quad 0, \qquad u < D(E)$$

$$= \quad C(E), \quad u > D(E). \quad (6)$$

It is important to note that this expression for $\sigma(u, E)$ imposes no quantization conditions on $D(E)$, thereby allowing it to be continuously variable as seemed to be indicated by the experiment. Purely rotational excitation would therefore be one possible cause of the cross-section enhancement.

If one considers vibrational excitation only, the weight of the state with vibrational quantum number, v, is $w_v = 1$, and in the harmonic oscillator approximation $u_v = (v + \frac{1}{2})h\nu$ so that Eq. (4) becomes

$$Q(E, T) = \frac{\sum_0^\infty \sigma_v(E) \exp(-vh\nu/kT)}{\sum_0^\infty \exp(-vh\nu/kT)}$$

$$= [1 - \exp(-h\nu/kT)] \sum_0^\infty \sigma_v(E) \exp(-vh\nu/kT). \quad (7)$$

Strictly speaking this form cannot yield straight-line Arrhenius plots. However, because the sum would give a concave upward plot on a semilog plot of Q versus $1/T$, while the term in parenthesis gives a concave downward contribution, the difference between the plotted curve and a straight line could escape notice, particularly over a range of temperature as limited as the one of the present experiments. Further, by varying the values of several σ_v's with electron energy, the apparent straight lines on the Arrhenius plots could seem to vary continuously with energy. Thus the possibility that only vibration energy is responsible for the observed phenomenon could not be excluded on experimental grounds.

Demkov's suggestion[3] and O'Malley's more detailed theory[5] ascribe the phenomenon to vibrational excitation. However, a separate direct experimental test can be, and was, made. This test involved studying the enhancement of cross section as a function of pressure in the oxygen oven.

IV. HIGH-PRESSURE EXPERIMENTS

When a gas expands from a high-pressure source as a beam into vacuum, the random thermal energy is partially converted into energy of directed motion and a reduction of temperature, as described in terms of molecular velocities referred to coordinates moving with the stream, occurs. Ashkenas and Sherman[10] have determined that the temperature along the beam axis of a gas emerging from a circular aperture is well described after moving several aperture diameters downstream by

$$T = \frac{T_0}{1 + \frac{1}{2}(\gamma - 1) G^2 (r/d)^{2(\gamma - 1)}} = \frac{T_0}{1 + \frac{1}{2} M^2 (\gamma - 1)}, \quad (8)$$

where T_0 is the initial temperature of the gas in the source, r is the distance downstream, d is the aperture diameter, γ is the ratio of specific heats at constant pressure and at constant volume, and G is a constant whose value is 3.65 if $\gamma = \frac{7}{5}$ and 3.96 if $\gamma = \frac{9}{7}$. M is the local Mach number at r. This result can be understood on the basis of an adiabatic, isentropic expansion of an ideal gas converting random energy into directed energy. In such an expansion the number density,

which is directly related to the temperature drop, diminishes with the inverse square of the distance along the axis from the aperture.

Equation (8) would be expected to hold as long as the gas can be treated as a continuous medium and molecular collisions occur sufficiently frequently to keep the gas in quasiequilibrium as it expands. At some point in the expansion, however, molecular collisions become insufficiently frequent to maintain quasiequilibrium, and the thermodynamic parameters of the gas, i.e., temperature, Mach number, etc., assume terminal values and are said to be frozen in. To estimate these one can take them to be the values at a time t_c, where t_c is the time after which the probability of a molecule having no further collisions becomes a reasonable fraction of unity. It then can be argued that the terminal Mach number, M_∞, is related to the inverse Knudsen number at the source, $\epsilon = d/\lambda_0$, where λ_0 is the mean free path at the aperture, by

$$M_\infty \propto \epsilon^{(\gamma - 1)/\gamma} . \tag{9}$$

In studying the inert gases for which $\gamma = \frac{5}{3}$, Anderson, Andres, Fenn, and Maise[11] have verified expression (9) for values of ϵ in excess of about 50. Scott and Phipps[12] have shown experimentally that for values of ϵ ranging from about 1 through 20, M_∞ is somewhat more strongly dependent on ϵ than given in (9) and is better described for the inert gases by $M_\infty \propto \epsilon^{0.65}$. Since the terminal temperature is related to the terminal Mach number in the ideal case by Eq. (8), the terminal temperature should be given by

$$T_\infty \cong T_0/(1 + a\epsilon^{2b}) , \tag{10}$$

where a is a constant and $b = (\gamma - 1)/\gamma$ for $\epsilon \gtrsim 50$ and $b \cong 0.65$ for $\epsilon \lesssim 20$.

When the gas has internal energy modes other than translation, the situation becomes more complex. For homonuclear diatomic molecular gases the interchange between translation energy and vibrational energy[13] is orders of magnitude less efficient than for translational energy exchange, and vibrational temperature is frozen in almost from the beginning of an expansion. Exchange between rotational energy and translational energy is rather rapid, although not as efficient as purely translational energy exchange, so that rotational temperature freezes in only slightly ahead of translational temperature. Knuth,[14] Miller,[15] and Willis and Hamel[16] have studied extensively rotational and translational energy exchange in freely expanding jets and have found that the terminal rotational temperature is very close to the terminal translation temperature.

For the present purposes, however, the most relevant experiments are those of P. V. Marrone,[17]

who studied rotational temperature alone in freely expanding jets of N_2. By observing the rotational structure in the emission from the first negative system of N_2^+ excited by an electron beam intersecting the jet at various points along its length, he was able to map the rotational temperature as a function of distance, arriving at terminal values of rotational temperature. He was also able to establish that these rotational temperature versus distance curves depended on the product of source pressure times aperture diameter, i.e., on ϵ, for values of $p_0 d$ from 15 to 480 Torr mm. Attempting to fit his data to an expression of the form given in Eq. (10), one finds that for the lower $p_0 d$ values of his measurements $b = 0.6 \pm 0.1$ (which is reminiscent of the translational temperature results of Scott and Phipps[12] for low values of ϵ) and $a \approx 1$ when ϵ is replaced by $p_0 d$ values in Torr mm.

The similarity of N_2 and O_2 for energy exchange between various internal energy modes suggests that the results of Marrone should fairly closely describe the situation with oxygen, i.e., that for low values of $p_0 d$ vibrational temperature should be frozen in from the beginning of an expansion and that the terminal rotational temperature should be given by

$$T_\infty \cong T_0/[1 + (p_0 d)^{0.6}] . \tag{11}$$

For a value of $p_0 d$ of 5 Torr mm, and an initial temperature of 2000°K, a terminal rotational temperature of about 600°K would be expected.

It should therefore be possible to determine experimentally whether or not rotational excitation was essential to the dissociative attachment cross-section enhancement by comparing results from two furnaces, the first with a large aperture operating at low pressures where effusive flow obtains and the vibrational and rotational temperature in the beam are the same, and the second with a small aperture operating at high pressures so that the vibrational temperature in the beam would be near the furnace temperature but the rotational temperature would be greatly reduced.

When such experiments were carried out, the results were as shown in Fig. 3, irrespective of the furnace pressure and aperture diameter for values of $p_0 d$ up to about 5 Torr mm, the maximum used in these experiments.

While the arguments leading to estimates of rotational temperature in our case are extremely crude and rely on extrapolation of data of Marrone on N_2 to the case of O_2 and extrapolation to values of $p_0 d$ below the range of his experiments, we feel that the results are significant. The weight of argument clearly points to a substantial rotational cooling (of the order of 1000°K or more). If rotational energy (and therefore rotational tem-

perature) alone were responsible for the shift of the O^- production curve with temperature, a rotational cooling of 200°K would have been readily discernible. The absence of a shift with the much higher cooling is strong evidence that vibrational energy is the essential form of energy, in keeping with the theory of Demkov and O'Malley.

V. AFFINITY OF O^-

Before the appearance of O'Malley's theory, among the speculations made by us as to the cause of the observed effects was one involving the possibility that the state of O^- for which the affinity 1.465 eV had been determined might not be the ground state of the ion. Observing the approximate linearity of the activation energy $D(E)$ with electron energy (Fig. 5) and extrapolating linearly to the zero-electron-energy activation energy $D(E)$ = $\mathfrak{D}-A$, where $\mathfrak{D}$ is the ground-state dissociation energy of O_2, the possibility of an O^- state with an affinity of $A = \mathfrak{D} - D(0) = 5.08 - \sim 1.98 \cong 3.10$ eV was suggested.

At the time, this suggestion was not entirely ludicrous because the photon energy in the photodetachment experiments had not reached this high and it was not impossible that the experiments of Branscomb et al.[1] had been dealing with an excited state of the O^- ion. Under the circumstances it seemed appropriate to make an equilibrium measurement of the affinity of ground-state O^- ions.

In this type of experiment as applied to the present case it is assumed that inside the iridium furnace equilibrium obtains between the oxygen atoms, the oxygen molecules, and the thermionic electrons. The equilibrium equations can be written down.

$$[O]^2/[O_2] = F_1(T)\exp(-\mathfrak{D}/kT), \qquad (12A)$$

$$[O][e]/[O^-] = F_2(T)\exp(-A/kT), \qquad (12B)$$

where the square brackets indicate the number densities of the constituents indicated, $\mathfrak{D}$ is the ground-state dissociation energy of the molecule, A is the affinity of the O^- ion, and $F_1(T)$ and $F_2(T)$ are the known partition function ratios. The electron density is given by

$$[e] = F_3(T)\exp(-W/kT), \qquad (13)$$

where W is the work function of iridium, when alteration of electron density due to space charge can be neglected.

Combining these three equations the O^- density in the furnace will be given by

$$[O^-] = \frac{F_3}{F_2}\,(F_1[O_2])^{1/2}\exp\left(\frac{-(\tfrac{1}{2}\mathfrak{D}+W-A)}{kT}\right). \qquad (14)$$

The negative ion current I^- carried by O^- ions effusing out of an aperture in the furnace will be given by $I^- = a[O^-]T^{1/2}$ where a is a constant. It follows that

$$I^- = aT^{1/2}\frac{F_3}{F_2}\,(F_1[O_2])^{1/2}\exp\left[-(\tfrac{1}{2}\mathfrak{D}+W-A)/kT\right]. \quad (15)$$

It is possible to select gas flows through the furnace such that the pressure is sufficiently high that there is negligible dissociation at temperatures near 2000°K and yet sufficiently low that the flow of gas through the aperture is effectively effusive. Under these conditions $[O_2] = bT^{-1/2}$, where b is a constant. Since the temperature dependence of both F_3 and F_2 is as $T^{3/2}$, their ratio is temperature-independent. If one neglects the contribution of all molecular states except the ground-state (which at temperatures of 2000°K is justifiable to about 1 part in 10^3), then

$$F_1 = gT^{1/2}[1 - \exp(-h\nu/kT)],$$

where g is a constant and $h\nu$ is the vibrational energy-level spacing. Inserting these temperature dependences into Eq. (15), it can be shown that the slope on a plot of $\log I^-$ versus $1/kT$ is given by

$$\frac{d(\ln I^-)}{d(1/kT)} = -(\tfrac{1}{2}\mathfrak{D}+W-A) - \tfrac{1}{2}kT +\frac{\tfrac{1}{2}h\nu}{\exp(h\nu/kT) - 1}\cdot (16)$$

In evaluating A from the slope observed in an experiment it is necessary to know the work function W. In the present case this was obtained by measuring the saturated electron currents drawn from the outer surface of the iridium furnace as a function of temperature. The saturated current, I_S, is given by the Richardson Dushman expression

$$I_S = gT^2\exp(-W/kT), \qquad (17)$$

where g is a constant. Since the work function of interest is that of iridium in an oxygen environment, the measurements were made with varying amounts of oxygen gas purposely admitted to the vacuum chamber housing the furnace. It was found that in the temperature range 1800–2100°K the value of W increased from 4.48 ± 0.20 to 5.18 ± 0.10 as oxygen was added to the background vacuum and appeared to stabilize at the higher value when presumably the iridium was fully oxygenated.

In measuring the O^- ion currents, the experimental arrangement was modified to that shown in Fig. 6. Ions emerged from the furnace which was biased negatively with respect to ground and then were accelerated and focussed by three aper-
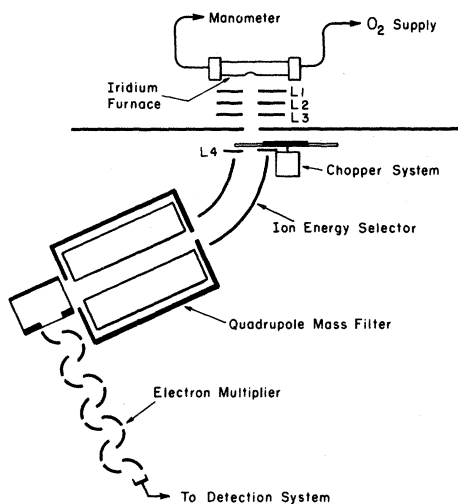
FIG. 6. Schematic of the experiment to determine the electron affinity of ground-state O^- ions using thermal equilibrium techniques.

ture lenses through the aperture separating the differentially pumped vacuum chambers. The mechanical chopper interrupted the ion beam thus generating ac signals for convenience of the electronics used. The ions were then deflected by a transverse electrostatic field and entered the mass filter. The deflection was necessary in view of the finding that with the mass filter on axis spurious signals appeared. These spurious signals were traced to negative ions after acceleration undergoing electron loss collisions in the background gas of the first chamber and being converted into positive ions. Those ions that were formed in the vicinity of L_1, which was positive with respect to ground, were accelerated into the mass filter, transmitted (since the mass filter does not distinguish between signs of charge), struck surfaces after emerging from the mass filter and emitted secondary electrons which were then drawn to the multiplier detector. Insertion of the electrostatic field and offsetting the mass filter ensured that all such positive ions would be prevented from reaching the mass filter.

Additionally the deflection field served as an energy selector for the negative ions. As such it allowed only O^- arriving from the furnace to enter the mass filter and excluded any negative ions that would be made by charge transfer along the ion path and therefore enter the second chamber at different energies than those coming from the furnace.

It was found that the value of the slope of the graph of $\log I^-$ versus $1/kT$ in the temperature range 1800–2100°K was -6.45 ± 0.10 eV. Using the mean temperature of this range for evaluation of the last two terms in Eq. (16), using the known spectroscopic values for $\mathfrak{D}$ (5.08 eV) and

$h\nu$ (0.196 eV), and using the determined value of W (5.18 ± 0.10 eV), the value of the affinity of ground-state O^- was given by Eq. (16) to be 1.31 ± 0.15 eV. The possibility of small systematic errors in temperature measurement exists and this result is regarded to be agreement with the more precisely determined photodetachment value of 1.465 eV.

In the interests of completeness we would point out that while the thermal equilibrium experiments were in progress, Branscomb, Smith, and Tissone[18] extended the energy range of the photodetachment experiments on O^- to 4 eV and found a photodetachment process occurring at an energy of 3.43 eV. Although this result could have been interpreted in terms of an O^- state with this affinity lying below the state whose affinity had previously been measured at 1.465 eV, the energy at which the newer photodetachment process appeared led those authors to interpret the result as detaching the electron and leaving the atom in the ^1D first excited state. The equilibrium measurement reported here, verifying that ground-state O^- has the 1.465 eV affinity value removes any doubt that the interpretation given by Branscomb, Smith, and Tissone is correct.

VI. SUMMARY AND CONCLUSIONS

The enhancement of the cross section for dissociative attachment in collisions of electrons with oxygen molecules is well established. Thermal equilibrium affinity measurements of the affinity of O^- confirm that the value accepted for the affinity is indeed associated with ground-state of the ion, thus obviating one tentatively held explanation of the effect. Experiments using heated oxygen beams from high-pressure molecular-beam sources where free jet expansion became operative strongly indicate that the form of internal energy responsible for the effect is vibrational energy.

These direct experimental findings support the theory of the effect as presented by O'Malley[5] and furthermore confirm the absolute cross sections predicted in his theory.

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Angular Distribution of Protons from Collisional Dissociation of H_2^+. I.

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The theory of the angular distribution of H_2^+ dissociation fragments resulting from H_2^+ collisions with neutral or charged targets is developed in the Born approximation. Earlier formulations of the problem are corrected and generalized. Calculations of the angular distributions for collisions which leave the H_2^+ in the $2p\sigma_u$, $2s\sigma_g$, and $2p\pi_u$ electronic states are carried out for He and Ar targets. It is assumed that the target either remains in its ground electronic state or undergoes an allowed transition. It is shown that the angular distributions vary considerably with the final H_2^+ electronic state considered, with the final kinetic energy of the H_2^+ fragments, with the final state of the target, and with the H_2^+ impact energy. Angular distributions for transitions to highly excited and ionized states of H_2^+ are considered in a qualitative way.

I. INTRODUCTION

In the past three years several measurements of the relative angular distribution of the protons resulting from H_2^+ dissociation during collisions with neutral targets have been reported.[1-5] In the more recent experiments the velocity distribution of the protons was also measured. The angular distributions, particularly when transformed to the center of mass (c. m.) frame of H_2^+, are markedly anisotropic and change their angular dependence rather rapidly as the final c. m.