

## Three-Body Attachment in $O_2$ Using Electron Beams\*

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The three-body attachment reaction in  $O_2$ ,  $e+2O_2 \rightarrow O_2^-+O_2$ , is studied by electron-beam techniques. Whereas swarm experiments show a smooth variation of the attachment coefficient with energy, the present electron-beam experiment shows pronounced structure. The peaks of this structure occur at the positions of the vibrational levels of the  $O_2^-$  system, which serve as compound states and have been identified in a previous experiment. These compound states dominate the low-energy cross sections in  $O_2$ . They can decay by autodetachment, thus accounting for the bulk of the vibrational cross sections in  $O_2$  at low energy; alternatively, they can be stabilized by a subsequent collision, thus leading to the formation of stable  $O_2^-$ . Thus we establish clearly that three-body attachment in  $O_2$  is a two-stage process and that the intermediate is a vibrationally excited state of  $O_2^-$ . We also obtain the temperature dependence of the three-body attachment coefficient and we discuss the anomalous behavior at higher pressures. The experimental observations are in excellent agreement with the theory of Chapman and Herzenberg.

### I. INTRODUCTION

The capture of free electrons by molecular oxygen leading to the formation of stable molecular negative ions is one of the more important processes leading to removal of thermal electrons from the upper atmosphere. Indeed, in certain atmospheric plasmas, this is the dominant electron-removal mechanism, and a complete understanding of this mechanism is of interest.

The attachment of low-energy (0–1 eV) electrons to molecular oxygen has been the subject of intensive study over a period of 40 years, and a wealth of experimental and theoretical data is available. However, it is only in recent years that an understanding of the attachment process has come about.<sup>1–4</sup>

In the present experiments we study the electron-attachment process at low electron energies (0–1 eV) over a wide range of target-gas temperatures using monoenergetic electrons. By the use of a monoenergetic electron beam we are able to study details of the attachment process hitherto unobservable. The use of high target-gas temperatures enables us to study the thermal effect on the attachment process. This latter consideration is of great importance, as molecular oxygen in the upper atmosphere is often at a high kinetic temperature and may be in a state of vibrational excitation.

Previous data and proposed mechanisms for electron attachment are reviewed in Sec. II. In Secs. III and IV we discuss the apparatus and the acquisition of data. The experimental results are presented in Sec. V together with a comparison of the latest theoretical work.

### II. SUMMARY OF PREVIOUS WORK

It is now well known that electron attachment to

molecular oxygen at low incident electron energies leading to the formation of  $O_2^-$  is a three-body process, which proceeds in two stages. In the first stage, the electron is captured by the molecule into a vibrationally excited temporary negative-ion state, sometimes called a compound or resonant state; i. e.,  $O_2+e \rightarrow O_2^{-*}$ . This excited molecular ion may subsequently autoionize into a free electron and a neutral molecule which may be left in a vibrationally excited state  $O_2^{-*} \rightarrow O_2(v)+e$ . Alternatively, the excess energy of the molecular ion may be removed in a collision with a third body, which in the case of pure oxygen is another  $O_2$  molecule; i. e.,  $O_2^{-*}+O_2 \rightarrow O_2^-(\text{stable})+O_2+KE$ . Such a two-stage process was first proposed by Bloch and Bradbury.<sup>5</sup> They assumed that the potential-energy curves of the neutral molecule and the molecular ion differed only in a vertical displacement, thus implying that the vibrational spacings of the neutral molecule and molecular ion are identical. This restriction implies that electron capture can only occur by non-adiabatic coupling involving the nuclear velocities. If electron capture occurs through nonadiabatic coupling, only the first vibrationally excited state of the molecular ion can be excited with a high probability. This level must be above the ground state of  $O_2$ , so the electron affinity of molecular oxygen cannot exceed the vibrational spacing of the neutral molecule. The Bloch-Bradbury theory further implies that electron attachment should occur only at a unique value of incident electron energy, and the attachment coefficient as a function of energy should consist of a single sharp line.

Many early experiments<sup>6–8</sup> indicated that the attachment process exhibited a two-body pressure dependence. Because of this evidence, Bloch and Bradbury had to assume that the lifetime of the excited state of  $O_2^-$  involved was much larger than

the time between molecular collisions so that most of the excited molecular ions would become stabilized.

Chanin, Phelps, and Biondi<sup>1</sup> showed conclusively from swarm experiments that at low electron energies attachment exhibits a three-body pressure dependence at least up to 150 mm; i. e., O<sub>2</sub><sup>-</sup> production varies quadratically as the gas pressure. This was verified by Schulz<sup>9</sup> using an electron-beam technique. From these measurements Chanin *et al.* estimated that the lifetimes of the excited O<sub>2</sub><sup>-</sup> state was between 10<sup>-10</sup> and 5 × 10<sup>-12</sup> sec, much less than assumed in the Bloch-Bradbury theory. Further, Pack and Phelps<sup>3</sup> have determined the electron affinity of O<sub>2</sub> to be 0.43 ± 0.02 eV. This value of the electron affinity has recently been confirmed by Cellota *et al.*<sup>10</sup> using a photoionization technique and by Compton<sup>11</sup> using a charge-exchange method. This value of the electron affinity implies that vibrational levels of the O<sub>2</sub><sup>-</sup> state higher than *v* = 1 must play a role in the attachment mechanism, destroying the simple Bloch-Bradbury model of a vertical displacement of the potential curves.

In a recent theoretical treatment of three-body attachment in oxygen, Herzenberg<sup>12</sup> treated the problem differently in two respects. (i) He removed the unphysical restriction that the spatial separations of the nuclei are the same at the minima of the potential curves in the ion and neutral molecule. The removal of this restriction makes possible the capture of the electron into more than only the first vibrational level of the ion through the much simpler mechanism of adiabatic coupling. (ii) Herzenberg described the initial electron-capture process in terms of a Breit-Wigner<sup>13</sup> formula. The Breit-Wigner formula is a general expression for the energy dependence of a cross section in the region of a resonant or temporary negative-ion state. The use of the Breit-Wigner formula avoids a detailed description of the actual capture mechanism, thus simplifying the problem.

In order to calculate the rate of formation of stable O<sub>2</sub><sup>-</sup>, it is necessary to take the product of three terms; viz., (i) the rate of formation of the excited negative-ion states, (ii) the probability that an ion will make a collision with a neutral particle before decaying, and (iii) the probability that such a collision will be a stabilizing one. Herzenberg treated the collision of the ion and molecule as being one of the spiralling type first described by Langevin. Herzenberg finds that the rate constant *K* can be written as<sup>14</sup>

$$K(E) = \frac{8}{3} (\pi^3 \hbar^2/m) (\alpha e^2/M)^{1/2} \xi \times \sum_{v'} f(E^{v'}, E) \lambda(E^{v'}) (\Gamma_v^{v'}/\Gamma^{v'}). \quad (1)$$

The symbol *v'* refers to a vibrational state of O<sub>2</sub><sup>-</sup>,

and *v* designates a vibrational state of O<sub>2</sub>. The term  $\Gamma_v^{v'}$  is the entry width from state *v* of O<sub>2</sub> to state *v'* of O<sub>2</sub><sup>-</sup>, and  $\Gamma^{v'}$  is the total width of state *v'*. The term  $(\alpha e^2/M)^{1/2}$  describes the long-range polarization interaction between the ion and molecule, where  $\alpha$  is the polarizability and  $\xi$  is the probability that the collision of O<sub>2</sub> and O<sub>2</sub><sup>-\*</sup> will be a stabilizing one. The reduced wavelength of the incident electron in the region of a resonance *v'* is  $\lambda(E^{v'})$ , and  $f(E^{v'}, E)$  is the value of the incident electron energy distribution at the resonance energy  $E^{v'}$ , where the mean electron energy is *E*. From theoretical considerations, Herzenberg concludes that  $\xi$  is of the order of unity for the low-lying resonances.

The vibrational spacings of the O<sub>2</sub><sup>-</sup> system are now well established,<sup>10,15-18</sup> and the vibrational levels of the O<sub>2</sub><sup>-</sup> system have been accurately fixed with respect to those of the neutral molecule.<sup>16,17</sup> The lifetimes of the *lowest few levels* of O<sub>2</sub><sup>-\*</sup> above *v* = 0 of O<sub>2</sub> are believed to be of the order of 10<sup>-10</sup> sec.<sup>12</sup> Further, it is known that the separation of nuclei in the ion and molecule are different at the minima of the potential curves.<sup>10,12,19</sup> From this evidence one would expect the rate constant for O<sub>2</sub><sup>-</sup> production to consist of a series of spikes, which occur at the energies of the vibrational levels of O<sub>2</sub><sup>-</sup> above *v* = 0 of the neutral molecule. That these spikes have never previously been observed is hardly surprising in view of the narrow energy distribution necessary to resolve them (which usually implies small primary electron-beam current) combined with the need to operate at relatively high pressure.

### III. APPARATUS

Figure 1 is a schematic diagram of the experimental tube used in the present experiments. This tube has been described in detail previously<sup>20</sup> and only a brief description will be given here.

Electrons are emitted from a directly heated thoria-coated iridium filament, and the effective width of the electron energy distribution is reduced to about 80–100 meV by the retarding-potential-difference method.<sup>21</sup> The electron beam is confined by a magnetic field, which in the present experiments is about 1000 G.

The collision chamber consists of an iridium cylinder which can be heated by the passage of a direct current. Inside the collision chamber are mounted a pair of parallel iridium plates which serve as collectors. The experimental tube, with the exception of the iridium parts, is gold plated to minimize contact potential differences. After baking at 300 °C for 24 h the background pressure in the vacuum system is of the order of 5 × 10<sup>-9</sup> Torr.

Negative ions produced in the collision chamber

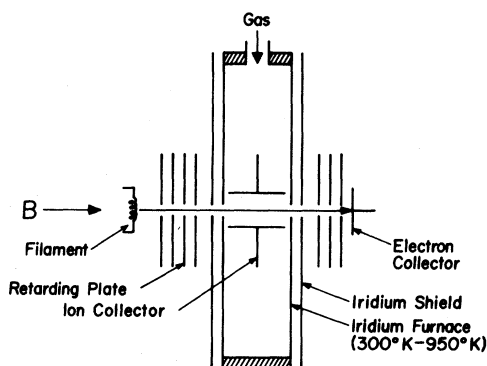


FIG. 1. Schematic diagram of the apparatus.

are extracted by maintaining an electric field between the parallel-plate collectors. The collected current is measured by a vibrating reed electrometer and stored in a multichannel analyzer. The potential on the retarding electrode of the electron gun and the add/subtract circuit of the multichannel analyzer are switched at the beginning of alternate scans in a mode similar to that described by Chantry<sup>22</sup> to give automatic data recording. The primary electron-beam current is typically  $1.0\text{--}5.0 \times 10^{-9}$  A.

#### IV. ACQUISITION OF DATA

The rate constant  $K$  for the attachment of electrons to  $O_2$  in a three-body process may be written as  $K = (Q_{\text{eff}} v/N)$ . Here,  $Q_{\text{eff}}$  is an effective cross section for the production of stable  $O_2^-$  governed by the relation  $i(O_2^-) = i_0 N Q_{\text{eff}} L$ , where  $N$  is the gas density,  $L$  is the length of the chamber,  $i_0$  is the primary electron current,  $i(O_2^-)$  is the negative-ion current, and  $v$  is the electron velocity. In the present apparatus there is no provision for direct measurement of the gas density in the collision chamber. The average gas density along the collision path is calculated from measurements of positive and negative ions produced by known electron currents, the relevant ionization<sup>23</sup> and dissociative-attachment<sup>20</sup> cross sections being known. The density is also measured by electron-beam attenuation experiments. The density data obtained in this way are plotted against the background pressure in the vacuum chamber. The background pressure and the density in the collision chamber are found to be directly related over a range of five orders of magnitude in the background pressure, when slight corrections for multiple electron scattering<sup>24</sup> in the collision chamber are made at the highest gas densities. The ratio of gas density in the collision chamber to that in the background is about 200.

The magnitude of  $Q_{\text{eff}}$  is determined by measuring the  $O_2^-$  current at low-incident electron

energy, and normalizing this signal against the  $O^-$  current produced from dissociative attachment in oxygen at 6.7 eV, using the same target-gas density and electron-beam current. The rate constant for  $O_2^-$  production peaks at about 0.1 eV, whereas the dissociative-attachment cross section for production of  $O^-$  peaks at an incident electron energy of 6.7 eV and has been measured in many independent experiments to be<sup>25</sup>  $1.30 \pm 0.05 \times 10^{-18}$  cm<sup>2</sup>. Since the rate of production of  $O_2^-$  varies quadratically with target-gas density and that for  $O^-$  varies linearly, the ratio of the two currents should vary linearly with density. Figure 2 shows a plot of the ratio of the negative-ion current at 0.1 eV to negative-ion current at 6.7 eV. The plot is seen to be linear over a wide range of target-gas densities, indicating that the peak at 0.1 eV does vary quadratically with the gas density and is indeed  $O_2^-$ .

Deviations from linearity occur when the target-gas density becomes greater than about  $4 \times 10^{15}$  cm<sup>-3</sup>. Above this density the collision number  $NQL$  (where  $N$  is the gas density,  $Q$  the elastic cross section for electrons, and  $L$  the collision-chamber length) becomes significantly greater than 1. Under such conditions a significant fraction of electrons make elastic collisions in the collision chamber, thus effectively increasing the path length over which the electrons may collide to form a negative ion. The theory of electron-gas collisions at intermediate and high gas pressures has been developed by Chantry, Phelps, and Schulz.<sup>24</sup> The equivalent

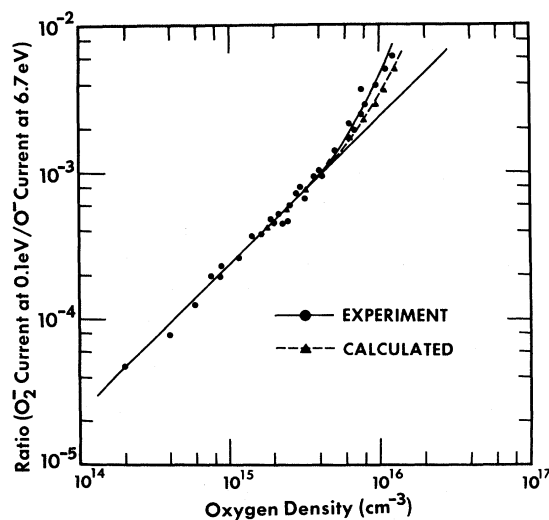


FIG. 2. Ratio of the  $O_2^-$  current at 0.1 eV to the  $O^-$  current at 6.7 eV, plotted as a function of target-gas density  $N$ . The linear plot shows that the  $O_2^-$  signal is dependent upon  $N^2$ . All measurements of the rate constant  $K$  were made at a target-gas density on the linear part of this plot.

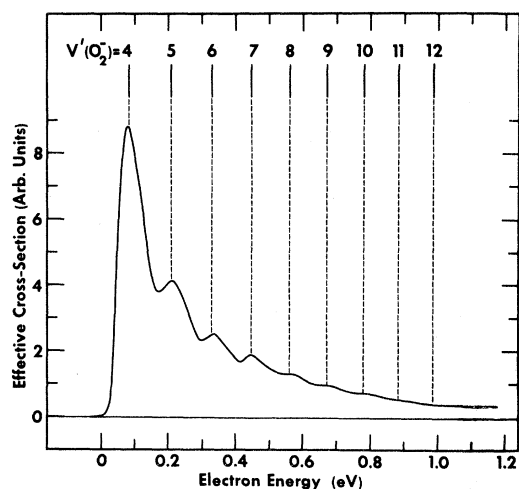


FIG. 3. Effective cross section for production of stable O<sub>2</sub><sup>-</sup> as a function of incident electron energy. The vibrational spacings of the O<sub>2</sub><sup>-</sup> system which were obtained in previous experiments are indicated at the top of the figure.

length factors  $g_1$  and  $g_2$  for the production of O<sub>2</sub><sup>-</sup> and O<sup>-</sup> at 0.1 and 6.7 eV, respectively, are obtained from Fig. 7 of Ref. 24. The elastic collision number is calculated using the elastic scattering cross section of Hake and Phelps<sup>26</sup> who obtained  $Q_{e\text{lastic}} = 4.4 \times 10^{-16}$  cm<sup>2</sup> at 0.1 eV and  $Q_{e\text{lastic}} = 6.4 \times 10^{-16}$  cm<sup>2</sup> at 6.7 eV. The ratio  $g_1/g_2$  is plotted as the dashed curve in Fig. 2 and is normalized to the linear part of the experimental curve. Although this theory indicates the correct density at which the deviations from linearity occur, the experimental and theoretical points do not exactly coincide. The equivalent-length factors are dependent upon the ratio  $1/m = \text{inelastic cross section} / \text{elastic cross section}$ . Chantry, Phelps, and Schulz plot the equivalent-length factors for  $1/m = 0, 0.01, \text{ and } 0.10$ . In estimating  $g_2$  for O<sup>-</sup> production at 6.7 eV we have used  $1/m = 0.01$ . The true value of  $1/m$  at this energy is 0.025. This results in a slight overestimate of  $g_2$  and a consequent underestimate in the ratio  $g_1/g_2$ , causing divergence between the experimental and calculated curves. The calculations do, however, explain qualitatively the divergence from linearity.

Negative ions are collected with a draw-out field sufficient to collect all the ions formed. Particular care is taken that no potential well occurs in the collision chamber when collecting the O<sub>2</sub><sup>-</sup> current. Such a potential well would result in the collection of elastically and inelastically scattered ("trapped")<sup>27</sup> electrons in addition to the true O<sub>2</sub><sup>-</sup> signal. The linearity of the plot in Fig. 2 is an indication that no such potential well exists. Effective cross sections measured with beam currents of  $1-5 \times 10^{-9}$  A are the same as those measured with beams of

$3 \times 10^{-8}$  A, indicating that any space-charge effects are negligible. The O<sub>2</sub><sup>-</sup> ions formed have very little kinetic energy, and quite low draw-out fields are sufficient to ensure saturation. Because of the low energy of the O<sub>2</sub><sup>-</sup> ions, care must be taken that the Larmor radius of the ions in the magnetic field is not less than the distance of the collection plate from the point of formation of the ions. If this were the case, O<sub>2</sub><sup>-</sup> ions would be lost to the side walls of the collision chamber. The effective cross section for electron attachment to O<sub>2</sub> is found to be independent of the magnetic field for values 500–1500 G. If the magnetic field is increased above 1500 G, a rapid decrease in the O<sub>2</sub><sup>-</sup> signal occurs.

## V. RESULTS

Figure 3 is a recorder tracing of the O<sub>2</sub><sup>-</sup> current as a function of electron energy. This trace represents the signal produced by the averaging of 256 successive electron-energy scans in the multichannel analyzer. The vibrational energy levels of the O<sub>2</sub><sup>-</sup> system with respect to the ground vibrational state of the neutral molecule have been determined previously<sup>16</sup> and are shown at the top of the figure. The experimental peaks in the effective O<sub>2</sub><sup>-</sup> cross section are seen to occur whenever the incident electron energy coincides with a vibrational level of the negative-ion system. The lifetimes of the lowest levels of the O<sub>2</sub><sup>-\*</sup> system above  $v' = 4$  are long ( $10^{-10}$  sec) and hence the widths of the levels are narrow, about 10  $\mu$ V. Consequently the effective cross section for O<sub>2</sub><sup>-</sup> production should consist of a series of spikes 10  $\mu$ V wide. The observed widths and the overlapping of the peaks in the present experiments are due entirely to the energy spread of the primary electron beam.

The rate constant in arbitrary units is calculated from the effective cross section of Fig. 3 by multiplying it by  $E^{1/2}$ , where  $E$  is the incident electron energy. The rate constant calculated in this way is plotted in Fig. 4. Also plotted in Fig. 4 is the maximum theoretical rate constant for three-body attachment calculated by Chapman and Herzberg<sup>4,14</sup> for a Gaussian electron energy distribution with a half-width of 110 mV. The experimental points have been normalized to the theoretical points at the second peak in the rate constant. The maximum theoretical rate constant is calculated from Eq. (1) by assuming that  $\xi$  (the probability that a collision between O<sub>2</sub><sup>-\*</sup> and O<sub>2</sub> will be a stabilizing one) is unity and independent of energy. In the calculations  $\Gamma_v^{v'}/\Gamma^{v'}$  the probability that an excited state  $v'$  of the ion will decay into a given state  $v$  of the molecule is obtained theoretically, and the resonance energies  $E^{v'}$  are obtained from experimental data. The agreement between the theory and the present experiment is seen to be particularly good

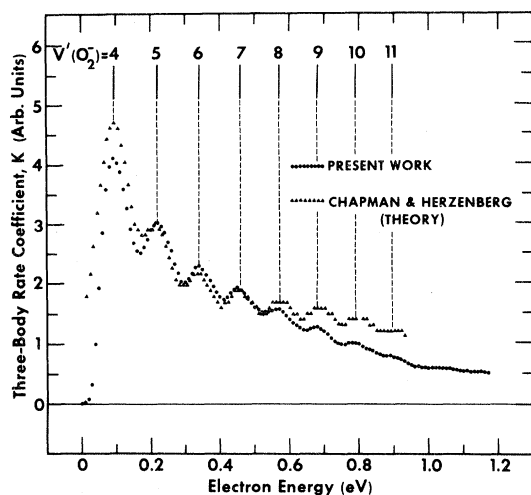


FIG. 4. Three-body rate constant  $K$  for production of  $O_2^-$  in pure  $O_2$ , in comparison with the theoretical data of Chapman and Herzberg, plotted as a function of incident electron energy. The present data and those of Chapman and Herzberg are normalized at the second peak. The vibrational spacing of the  $O_2^-$  system are indicated at the top of the figure.

at low energy; small deviations occur above about 0.6 eV. As pointed out to us by Herzberg, this deviation could result from a variation of the coefficient  $\xi$  with energy. One would expect that at higher incident energies (corresponding to the excitation of high levels of the  $O_2^-$  system), stabilization is more difficult because the  $O_2^-*$  system may still end up in an autoionizing state, and only particularly favorable events will lead to the formation of stable  $O_2^-$ . On the other hand, when the incident electron produces  $O_2^-$  in the fourth vibrational state, most collisions are expected to be of the stabilizing kind. This effect, leading to a decrease in the stabilization coefficient with energy, is not included in the theory and could cause the discrepancy of Fig. 4.

The present data are compared with the swarm experiments of Pack and Phelps<sup>3</sup> in Fig. 5. Here we have normalized our data to those of Pack and Phelps<sup>3</sup> at the first peak. Figure 5 shows that although the electron energy spread in the swarm experiments is too large to resolve any structure, the swarm data do follow very closely the envelope of the present data. The swarm data are higher at higher energy, compared to the electron-beam data, because the electron energy distributions in the two types of experiment differ considerably. In a swarm experiment the electron energy spread is approximately equal to half the mean electron energy.

The absolute value of the rate constant is calculated from the data of Fig. 4 combined with

Fig. 3, the cross section for  $O^-/O_2$  production at 6.7 eV being known. The absolute rate constant at the peak which occurs at about 0.09 eV is found to be  $(5.6 \pm 1.3) \times 10^{-30}$  cm<sup>6</sup>/sec in the present work. This value is in very good agreement with that of Chanin, Phelps, and Biondi,<sup>1</sup> and of Pack and Phelps<sup>3</sup> who give a value of  $4.8 \times 10^{-30}$  cm<sup>6</sup>/sec. Both these experimental values are also in very good agreement with the maximum theoretical value of  $4.7 \times 10^{-30}$  cm<sup>6</sup>/sec calculated<sup>4</sup> for an electron energy distribution of 110 meV. The agreement between the experimental and theoretical value indicates that for at least the low vibrational levels of  $O_2^-$ , the probability  $\xi$  that a collision will be a stabilizing one, is indeed very close to unity. To obtain better agreement between theory and experiment at the higher energies would entail very much more complicated calculations.

## VI. TEMPERATURE DEPENDENCE

For measurements of the rate constant at high gas temperatures, the collision chamber is heated by passing a direct current through it. For a fixed rate of gas flow through the system, the density in the collision chamber falls as  $T^{-1/2}$ . For a fixed electron current, the flow rate of the gas is increased until the  $O^-$  current at 6.7 eV is the same as that produced at room temperature. This ensures that the gas density in the collision region remains constant as the gas temperature is increased. The cross section for  $O^-/O_2$  production at 6.7 eV is known to be essentially independent of gas temperature<sup>20,28</sup> in the range 300–1000 °K. Figure 5 shows a comparison of the present data

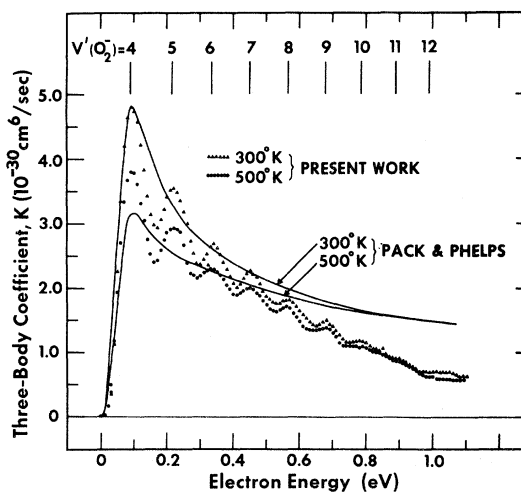


FIG. 5. Three-body rate constant  $K$  for production of  $O_2^-$  in pure  $O_2$  at 300 and 500 °K, normalized to the experimental data of Pack and Phelps at the peak of their 300 °K curve. The vibrational spacings of the  $O_2$  system are indicated at the top of the figure.

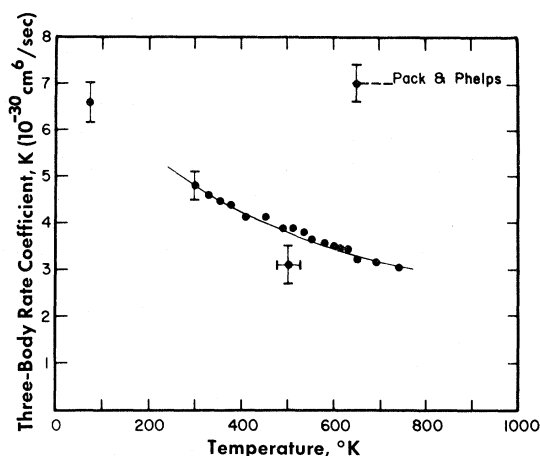


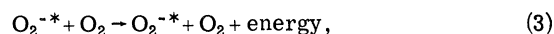
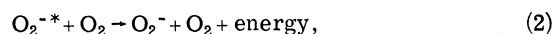
FIG. 6. Temperature dependence of the peak at 0.09 eV in the rate constant  $K$  for production of  $O_2^-$  in pure  $O_2$ , in comparison with the experiment of Pack and Phelps. The present data are normalized to those of Pack and Phelps at 300 °K.

and those of swarm experiments<sup>1,3</sup> at room temperature and at 500 °K. Although the swarm data fit the envelope of the present data very well at both temperatures, a larger temperature dependence of the first peak is indicated by the swarm experiments than in the present data. As mentioned earlier, the measured shape of the rate constant is a convolution of the electron energy spread with a set of narrow spikes, whose spacing is equal to the vibrational spacings of the negative-ion system. Consequently, the peak height of the measured signal will be critically dependent on the electron energy spread.<sup>29</sup>

In the present experiments only single collisions between the incident electrons and the target molecule occur, and thus the incident electron energy spread is not altered as the gas temperature increases. In swarm experiments the electrons make many collisions and the energy spread is increased by the thermal motions of the target gas. The increase in energy spread will therefore be greater at higher gas temperatures, leading to a decrease in the measured value of  $K$  at the peak. This effect may partially explain the discrepancy between the present data and those obtained from swarms.

Figure 6 shows a plot of the temperature dependence of the rate constant at the first peak. Also shown in Fig. 6 are the results of Pack and Phelps.<sup>3</sup> The present data are normalized to those of Pack and Phelps at 0.09 eV and 300 °K. In the present experiments it is not possible to extend measurements much above 750 °K, because thermal drifts in the feedthrough insulators of the collision chamber made long-term averaging of the very small  $O_2^-$  currents impossible.<sup>30</sup>

Both the present and the swarm data of Fig. 5 indicate that the temperature dependence of the rate constant becomes less pronounced as the energy increases. This is illustrated more clearly in Fig. 7, where we have plotted the fractional change in the rate constant as a function of gas temperature at electron energies of 0.09, 0.34, and 0.57 eV. These electron energies correspond to the energies of the  $v' = 4, 6,$  and  $8$  vibrational states of  $O_2^-$ . The reactions which can occur when an  $O_2^{-*}$  ion collides with a neutral  $O_2$  molecule are



Equation (2) is the stabilization process in which either  $O_2^-$  or  $O_2$  may be left excited, provided only that the negative ion is stable against emission of an electron. Equation (3) is elastic or inelastic scattering leaving  $O_2^{-*}$  with sufficient energy to emit an electron. Equation (4) is electron detachment, and can be a powerful reaction when the collision partners have sufficient energy.<sup>12</sup>

For a negative ion which is initially formed in a high vibrational state, thermal energy accounts for a very small fraction of the total energy. On the other hand, for an ion which is formed in a low vibrational level, say,  $v' = 4$ , the thermal energy accounts for a large fraction of the total energy.

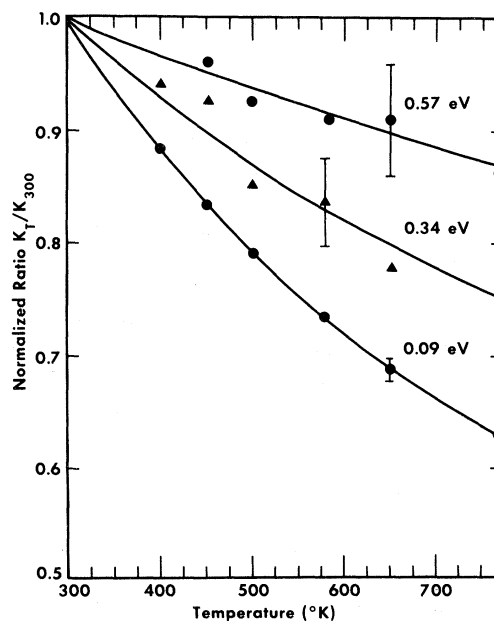


FIG. 7. Fractional variation of the three-body rate constant as a function of target-gas temperature. The data, which are plotted for three incident electron energies, show that the rate constant is less dependent on target-gas temperature at higher incident electron energy.

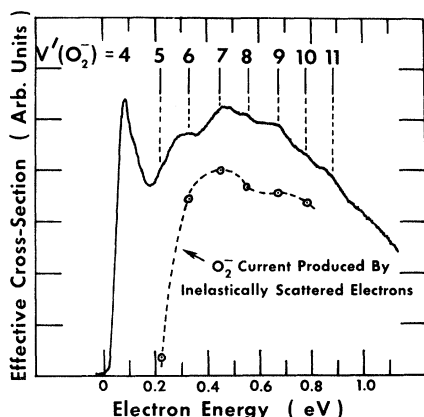


FIG. 8. Effective cross section for  $O_2^-$  production in pure  $O_2$  at high target-gas density as a function of incident electron energy. The data show a large "hump" centered around 0.6 eV. The lower (dashed) curve shows the calculated cross section for  $O_2^-$  production by electrons which have lost energy in making an inelastic collision. The vibrational spacings of the  $O_2^-$  system are indicated at the top of the figure.

It follows that electron detachment will be much more sensitive to changes in thermal energy at low electron energies than at higher electron energies.

#### VII. HIGH-PRESSURE MEASUREMENTS

At target-gas densities greater than about  $10^{15}$   $cm^{-3}$ , a large broad peak centered at about 0.6-eV incident electron energy is seen to appear on the effective cross section for  $O_2^-$  production. This broad peak, illustrated in Fig. 8 increases at a rate greater than the square of the gas density and has previously been observed by Schulz.<sup>31</sup> Such a peak is not observed in swarm experiments even at 100 times higher gas densities. Measurements of the ratio of the magnitude of the broad peak at 0.6 eV to the magnitude of the peak at about 0.1 eV exhibit a linear pressure dependence, as shown in Fig. 9. Since we have previously shown that the peak at 0.1 eV varies as  $N^2$ , Fig. 9 indicates that the peak at 0.6 eV varies as  $N^3$ . Measurements show that the ratio (peak 0.6 eV/peak 0.1 eV) is independent of the incident electron current.

There are at least two possible explanations for this broad peak.

(a) Oxygen at room temperature is able to form dimers, i. e.,  $O_2 + O_2 \rightarrow O_4$ . The rate constant of such a process is of course dependent on  $N^2$ . It is possible that an oxygen dimer so formed would undergo dissociative attachment by electron impact, leaving the molecular ion vibrationally excited, i. e.,  $O_4 + e \rightarrow O_2 + O_2^{-*}$ . This excited molecular ion could then be stabilized by a collision with another  $O_2$  molecule. Combinations of the two above processes would yield an  $O_2^-$  signal which varies as  $N^3$

consistent with our observations. However, such a process, if it exists, should be observed in swarm experiments, which is not the case. The binding energy of  $O_4$  is very small, and if the observed peak at 0.6 eV were due to the above process, it would disappear on heating the gas by a few hundred degrees by removing any  $O_4$ . It is found, however, that the magnitude of the  $O_2^-$  peak does not strongly depend on the gas temperature. This fact seems to rule out dimers as a cause for the 0.6-eV peak.

(b) If the incident electrons lose most of their energy in an inelastic collision with the target gas, they will then be able to participate in the usual three-body attachment process at low electron energy. Such a process can occur when the gas density is high enough to cause multiple scattering of the electrons, and the  $O_2^-$  current produced will then vary as  $N^3$ .

We have previously shown<sup>16</sup> that the vibrational excitation cross section of molecular oxygen consists of a series of spikes which are coincident in energy with the resonances (vibrational levels) in the negative-ion system. When an electron with initial energy  $V_0$  excites a vibrational state of oxygen via one of these negative-ion states, the electron is left with an energy  $E = (V_0 - V_x)$ , where  $V_x$  is the energy of the final vibrational state of the neutral molecule. Using the data of Ref. 16, Chapman and Herzenberg<sup>4</sup> have extended to higher energies the vibrational excitation cross section for  $v=1, 2$ , and 3 of  $O_2$ . Their data show that the envelope of the spikes for the  $v=1$  cross section has a maximum at about 0.6 eV, and for  $v=2$  at about 0.9 eV. This finding is in good agreement with the recently reported results of Linder and Schmidt<sup>17</sup> who observe experimentally that the envelope of the spikes for  $v=1$  peaks around 0.6 eV. We have used the data

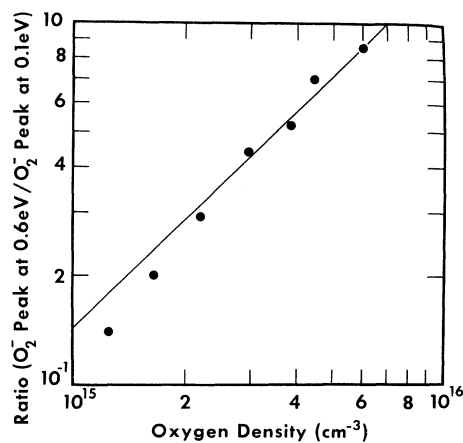


FIG. 9. Ratio of the  $O_2^-$  peak at 0.6 eV to the  $O_2^-$  peak at 0.1 eV. This plot indicates that the "hump" at 0.6 eV in Fig. 8 is dependent on the cube of the target-gas density.

of Chapman and Herzberg to calculate the relative fraction of the incident electrons which suffer a particular energy loss, i.e., the relative fractions of electrons whose final energy is  $(V_0 - V_x)$ . The relative current of O<sub>2</sub><sup>-</sup> produced in a three-body collision by these electrons which have energy  $V_0 - V_x$  is calculated by use of Fig. 3. The calculated current of O<sub>2</sub><sup>-</sup> produced by electrons which have suffered this energy-loss mechanism is shown in Fig. 8 by the dashed curve. This figure shows that the process described above predicts very well the observed shape of the effective O<sub>2</sub><sup>-</sup> cross section at high densities, and satisfies the required pressure dependence.

The process which we invoke for the explanation of the 0.6-eV peak in Fig. 8 is entirely analogous to the process described by Chantry<sup>32</sup> to explain the peaks which occur in the dissociative-attachment cross section in molecular oxygen at 15 eV. In dissociative attachment the observed signal is proportional to  $N^2$  whereas in our case it is proportional to  $N^3$ .

The above mechanism does not produce a peak at 0.6 eV in swarm experiments. In an electron-beam experiment the electrons in the collision chamber are not subject to any accelerating electric field along their path. Consequently, once an electron has lost energy in an inelastic collision, it may

fall into an energy range where three-body attachment is at its peak. In a swarm experiment the electrons are subject to a uniform accelerating field and thus continually gain energy from the field and lose energy in inelastic collision. After the first few-hundred collisions the electron energy distribution is independent of position.

### VIII. DISCUSSION

We have pointed out previously that electron-collision processes at low energies in diatomic molecules are dominated by the existence of the compound states. This paper points out that even three-body attachment processes must be interpreted in terms of these compound states. The parameters of the compound state in O<sub>2</sub> are now well enough known so that a meaningful theoretical treatment is possible. This task has been recently completed by Chapman and Herzberg, who could calculate both the vibrational cross sections and three-body attachment from the parameters of the compound state.

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be 132 meV and the anharmonicity of  $\hbar\omega_e x_e = 1.5$  meV.

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<sup>29</sup>Calculations by Chapman and Herzenberg show that for an electron energy distribution 70 meV wide, the spikes in the rate constant are entirely resolved, while for a distribution slightly more than double this width, 150 meV, any structure is completely smeared out, producing an envelope similar to that obtained by Pack and Phelps. Further, according to these calculations, the

first peak of  $K_{\max}$  is reduced from  $7.1 \times 10^{-30}$  cm<sup>6</sup>/sec for 70-meV energy spread, to  $3.9 \times 10^{-30}$  cm<sup>6</sup>/sec for 150-meV energy spread, illustrating the sensitivity of the measured value on the incident electron energy spread.

<sup>30</sup>The same apparatus has been used to measure the temperature dependence of other collision cross sections up to temperatures as high as 1300°K. However, in these cases the cross sections were larger and no signal averaging was required.

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PHYSICAL REVIEW A

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## Lifetimes, $g$ Factors, and Collision Cross Sections of Hydrogen Molecules in the $(1s3p) \ ^3\Pi_u$ Level

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Experimental results obtained by Hanle and Bitter-Brossel effects on the  $N=1$  and  $N=2$  ( $v=0, 1, 2$ , and  $3$ ) levels of the  $(1s3p) \ ^3\Pi_u$  state of the parahydrogen molecule excited by electron impact are presented. Resonances are found at the experimentally lowest possible frequencies (21–64 MHz) in a region where the  $\underline{N} \cdot \underline{S}$  decoupling is nonexistent for the  $N=2$  level [the measured Landé  $g$  factors are  $0.77 \pm 0.01$  and  $0.48 \pm 0.02$  corresponding to a pure Hund's-coupling case (b)] and just beginning for the  $N=1$  level (at 21 MHz the apparent measured  $g$  is  $1.235 \pm 0.01$ ). These results together with the calculations carried out in the case of complete  $\underline{N} \cdot \underline{S}$  coupling lead to lifetimes  $\tau = (3.10 \pm 0.3) \times 10^{-8}$  sec ( $N=1$ ) and  $\tau = (3.15 \pm 0.3) \times 10^{-8}$  sec ( $N=2$ ) and  $H_2^* - H_2$  cross sections  $\sigma = 232 \pm 30 \text{ \AA}^2$  ( $N=1$ ) and  $\sigma = 240 \pm 30 \text{ \AA}^2$  ( $N=2$ ). The quantities  $g$ ,  $\tau$ , and  $\sigma$  were all found to be independent on the vibrational number. Risk of cascade was eliminated.

### I. INTRODUCTION

Recently, methods used in atomic spectroscopy have been successfully extended to molecular spectroscopy. They consist in studying excited states by level-crossing<sup>1-9</sup> (Hanle effect<sup>10</sup>) and magnetic resonance<sup>11-14</sup> (Bitter-Brossel effect<sup>15</sup>). Both of these effects are due to an alignment of an excited level (the Zeeman sublevels of different  $|m|$  are inequally populated) created as described below by the excitation process. This alignment corresponds to a linear polarization of light emitted by this level (analogous effects exist in the case of circular polarization).

In the typical Hanle effect, one applies a static magnetic field at a right angle to the alignment direction (Fig. 1). In the classical explanation, the field produces a Larmor precession of the whole excited molecule, which, when averaged over the lifetime, gives a rotation of the plane of polarization and a partial depolarization of the emitted light. In the simple case where the fine and/or hyperfine coupling is not partially decoupled by the magnetic field (i. e., is either fully coupled, or fully decoupled), the width of the Hanle curve (per-

centage of polarization of the emitted light as a function of the magnetic field) gives the  $g\tau$  product ( $g$  is the Landé  $g$  factor and  $\tau$  the lifetime of the excited level).

In the typical Brossel effect, one applies a static magnetic field parallel to the alignment direction and a rf field perpendicular to the static field (Fig. 1). The polarization of the emitted light is determined by the difference of population of the Zeeman sublevels. When the frequency of the rf field is equal to the energy difference between the  $\Delta m = 1$  Zeeman sublevels (single-quantum resonance), transitions are induced between those sublevels. The resulting modification of population of the sublevels gives a modification of the polarization of the emitted light. In the absence of intermediate coupling, the position of the Brossel resonance gives the value of  $g$ .

A knowledge of  $g$  and  $\tau$  permits one to deduce the collision cross section  $\sigma$  from pressure broadening measurements of these curves and the coupling scheme of the angular moments. If magnetic resonance is carried out in the partial decoupling zone, fine or hyperfine structure can be determined.<sup>16</sup>

The first step in such an experiment is to excite