

## Excitation of Vibrational and Electronic Levels in O<sub>2</sub> by Electron Impact\*

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Low-energy inelastic collisions between electrons and oxygen molecules are studied using the trapped-electron method. Peaks in the trapped-electron current are interpreted as vibrational excitation of the oxygen molecule to the states  $v=1$  to  $v=8$ . Two of these peaks can be attributed in part to the excitation of the  ${}^1\Delta_g$  and  ${}^1\Sigma_g^+$  states. Approximate cross sections at 0.16 eV above threshold are less than  $3\times 10^{-20}$  and  $6\times 10^{-21}$  cm<sup>2</sup> for the  ${}^1\Delta_g$  and  ${}^1\Sigma_g^+$  states, respectively. For electronic states above 5 eV, the cross sections at 0.16 eV above threshold are of the order of  $10^{-18}$  cm<sup>2</sup>.

THE study of the vibrational excitation of the oxygen molecule has been undertaken in order to clarify the processes by which electrons excite vibrational levels in different molecules. Recently it has been shown<sup>1,2</sup> that vibrational excitation of the nitrogen molecule proceeds via the excitation of a temporary negative ion. On this model the incident electron excites the temporary negative ion, and the system decays into a free electron plus a nitrogen molecule in various states of vibrational excitation. In the case of nitrogen, this model explains the large vibrational excitation cross section observed, the unusually high energy at which the onset for vibrational excitation occurs (1.5 eV) and, qualitatively, the unusual energy dependence of the cross section for various vibrational states. Two methods of observation have been used for a study of the nitrogen molecule, namely, the trapped-electron method<sup>3</sup> and the double electrostatic analyzer.<sup>2</sup> The information obtainable using the double electrostatic analyzer is more extensive and in some respects more meaningful than that obtainable from the trapped-electron method. The former gives the energy dependence of the cross section to any resolved level, and the magnitude of the cross section relative to the elastic cross section if the scattering is isotropic.<sup>4</sup> The trapped-electron method shows the existence of inelastic processes and gives the value of the cross section a few tenths of an eV above threshold without angular discrimination. The trapped-electron method has a very high sensitivity; every inelastic collision registers by the arrival of an electron at the collector. The double electrostatic analyzer has a sensitivity about a factor 10<sup>4</sup> lower. Thus, when the cross section of an inelastic process is low, it is difficult at present to use the double electrostatic analyzer.

This paper discusses the results in oxygen using the

trapped-electron method. The cross sections of the low-energy inelastic processes are too small to be studied in the double electrostatic analyzer described in reference 2.

Very little information is available concerning the excitation of vibrational or electronic levels in O<sub>2</sub> by electron impact. Most of the data on vibrational excitation come from swarm experiments in the form of the fractional energy loss per collision, and it is generally difficult to extract information regarding vibrational cross sections and the number of vibrational states excited. Recently, Frost and Phelps<sup>5</sup> have shown that it is possible to determine the shape and magnitude of inelastic cross sections from swarm experiments and have obtained values for rotational and vibrational cross sections in H<sub>2</sub> and N<sub>2</sub>. However, no similar results are yet available for O<sub>2</sub>.

### I. EXPERIMENT

The trapped-electron method is used for this study. A detailed description of the method can be found in a paper by Schulz<sup>6</sup> so that only a brief review is presented here.

An electron beam aligned by a 1000-G permanent magnet traverses a region in which a potential well has been established. Those electrons in the beam which have made inelastic collisions such that their residual energy is less than the well depth are trapped in the potential well and collected on a cylindrical collector, separately from the main electron beam ("trapped-electron current"). The spread of electron energies in the beam is kept to about 0.15 to 0.2 eV total spread with a width at half maximum of about 0.07 to 0.1 eV by the use of the retarding potential difference method.<sup>7</sup>

The energy scale is established by electron retarding experiments and is accurate to about  $\pm 0.1$  eV, although

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<sup>1</sup> R. Haas, *Z. Physik* **148**, 177 (1957).

<sup>2</sup> G. J. Schulz, *Phys. Rev.* **125**, 229 (1962).

<sup>3</sup> G. J. Schulz, *Phys. Rev.* **116**, 1141 (1959).

<sup>4</sup> These data cannot be obtained in the double electrostatic analyzer as described in reference 2. However, if the scattered electrons are analyzed in a direction different from the forward direction, data on the relative cross sections at a particular angle can be readily obtained.

<sup>5</sup> L. S. Frost and A. V. Phelps, *Fifth International Conference on Ionization Phenomena in Gases, Munich, 1961* (North-Holland Publishing Company, Amsterdam, 1962), p. 192; and *Phys. Rev.* **127**, 1621, 1962.

<sup>6</sup> G. J. Schulz, *Phys. Rev.* **112**, 150 (1958).

<sup>7</sup> The energy spread of the electrons remained remarkably constant during the two months during which the bulk of the data were taken. During this period, the oxygen pressure was raised up to 0.1 mm Hg. The contact potential shift was found to be dependent only on the presence of oxygen in the system and its value (1.1 V) could be reproduced to better than 0.1 V. A thoria coated iridium filament was used and all electrodes in the gun, as well as the collision chamber, were gold plated. The electron collectors were coated with electrolytically deposited platinum black.

separation of peaks can be determined to a much higher accuracy. Reproducibility of peak separations is better than 0.02 eV.

There are four types of processes which lead to a current arriving at the collector for trapped electrons listed in the order in which they appear as the electron energy is increased.

(1) Trapping of electrons due to elastic scattering at zero accelerating voltage and persisting up to about 1.5 eV. This effect can be explained by considering that the electrons, after an elastic collision, have essentially an isotropic angular distribution. Thus, at low energies, most of the elastically scattered electrons have a component of velocity in the axial direction which is not sufficient to escape from the trap. Near zero accelerating voltage it takes a very improbable subsequent collision to direct the velocity in exactly the axial direction so that the electron can escape. With a small escape cone, a significant number of electrons can undergo the collisions necessary to diffuse across the magnetic field to the collector. At higher energies the escape cone becomes larger and the trapped-electron current due to elastic scattering disappears. For a study of inelastic processes occurring below 1.5 eV, this portion of the trapped-electron current is undesirable but it has not been possible to eliminate it. All inelastic processes occurring below 1.5 eV are therefore superimposed on this background. The variation of this portion of the trapped-electron current is a smooth function of electron energy for atomic gases and therefore any structure in the curve for molecular gases is interpreted as an inelastic process.<sup>8</sup>

(2) Trapping of electrons due to the excitation of vibrational states. This process can occur via an intermediate temporary negative ion state which decays into vibrationally excited states of the molecule plus an electron. This process has been previously observed for  $N_2$ ,  $CO^3$ ,  $N_2O$ ,<sup>9</sup> and  $COS$  and it is characterized by a large cross section in an energy range a few eV above the threshold of the vibrational levels.

(3) Trapping of electrons due to the excitation of electronic states of the molecule. This process has been previously studied, using the trapped-electron method, for  $H_2$ ,  $He$ ,  $Hg$ ,<sup>6</sup>  $N_2O$ ,<sup>9</sup> and  $H_2O$ .<sup>10</sup> The results in  $O_2$  are reported in Sec. III.

(4) Formation of negative ions which reach the collector in addition to the trapped-electron current. It is possible to measure the negative ion current separately by decreasing the well depth to essentially zero such that no trapping occurs and the negative ions reach the collector without interference with the trapped-electrons. This procedure has to be applied to the inter-

<sup>8</sup> There is also the possibility that the elastic cross section has structure in the energy range of a temporary negative ion. Because the discrimination against elastic processes is not complete below 1.5 eV, it is possible that elastic processes contribute to a small extent to the observed structure.

<sup>9</sup> G. J. Schulz, *J. Chem. Phys.* **34**, 1778 (1961).

<sup>10</sup> G. J. Schulz, *J. Chem. Phys.* **33**, 1661 (1960).

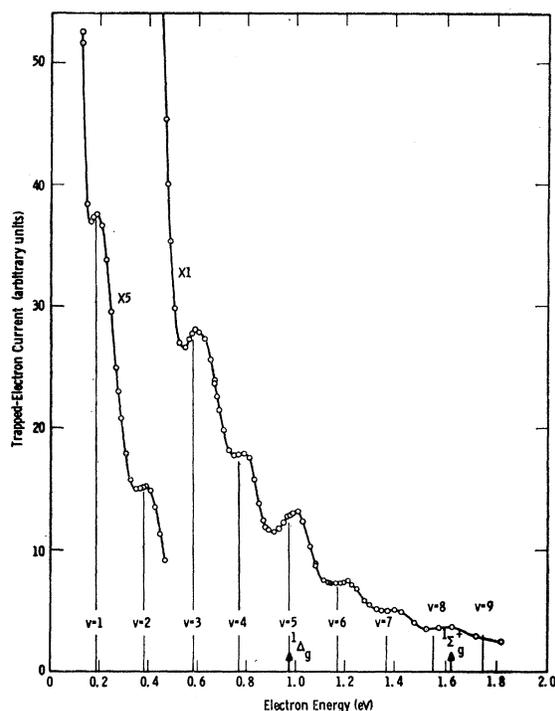


Fig. 1. Trapped-electron current vs electron energy in  $O_2$  below 2.0 eV. The vertical lines are drawn at the energies of the vibrational levels of  $O_2$ . Two low-lying electronic states,  $^1\Delta_g$  and  $^1\Sigma_g^+$  are indicated.

pretation of the results in the electronegative gases, such as  $O_2$ .

The background pressure in the vacuum system is of the order of  $5 \times 10^{-9}$  torr. In order to assure the purity of  $O_2$  in the system, differential pumping is used. The oxygen pressure in the collision chamber is varied from  $10^{-5}$  to  $5 \times 10^{-3}$  torr.

## II. VIBRATIONAL AND ELECTRONIC EXCITATION BELOW 2 eV

Figure 1 shows a plot of the trapped-electron current vs electron energy. The curve is interpreted as a superposition of the "elastic" component of the trapped-electron current discussed above and inelastic peaks. The same energy range was examined in helium and a smooth curve was found under identical operating conditions of mean-free path, current, and well depth. The electron energy scale is obtained from retarding curves on the electron beam. However, past experience has shown that the energy thus determined cannot be relied on to better than  $\pm 0.05$  to 0.1 eV. Thus, the energy scale can be shifted by at least  $\pm 0.05$  eV. However, the separation of the peaks is determined more accurately. The vibrational spacing of the low levels of the ground electronic state of  $O_2$  is 0.196 eV and vertical lines are drawn at the positions of the vibrational levels. Two known low-lying electronic states exist in  $O_2$ , namely, the  $^1\Delta_g$  state at 0.98 eV and the  $^1\Sigma_g^+$  state at 1.63 eV.

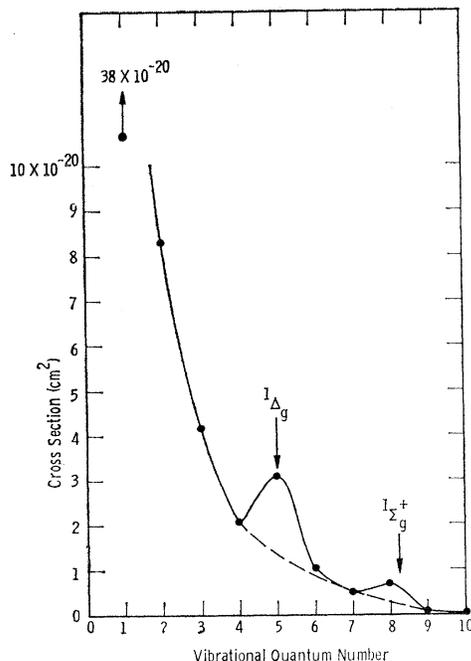


FIG. 2. Cross section at 0.16 eV above threshold vs vibrational quantum number in  $O_2$ .

The position of these states is also indicated in Fig. 1. The energy of the ground vibrational level for the  ${}^1\Delta_g$  state coincides within the resolution of the present experiment with the  $v=5$  level of the ground electronic state ( $X^3\Sigma_g^-$ ), and the  ${}^1\Sigma_g^+$  state is removed from the  $v=8$  level by only 0.07 eV. Thus, there is no hope of resolving the electronically excited states from the vibrational peaks of the  $X^3\Sigma_g^-$  state on the energy scale in the present experiment.

### III. CROSS SECTIONS

Absolute values of cross sections are determined by comparison with the peak of the dissociative negative ion formation at 6.7 eV. The cross section at the peak of the dissociative negative ion formation is  $1.3 \times 10^{-18}$   $cm^2$ ,<sup>11</sup> and the trapped-electron current can be normalized to this value. The well depth is reduced to essentially zero when the negative ion current is measured.

The peak of the trapped-electron current determines the cross section at an energy equal to the well depth above the onset of the inelastic process. One can obtain the peak value of the potential well from the shift of electron retarding curves with a potential "hump" instead of a well. However, the potential well is not constant but varies along the length of the collision chamber and thus the effective well depth is smaller than that determined from electron retarding curves.

<sup>11</sup> I. S. Buchelnikova, Soviet Phys.—JETP **35**, 783 (1959). The value of the negative ion cross section has been confirmed in a recent experiment [G. J. Schulz (to be published)].

The effective well depth is established from experiments in helium. The cross section, as well as the shape of the excitation curve of the  $2^3S$  state in helium, is well established.<sup>3</sup> Thus, by referring the trapped-electron current at the peak resulting from the excitation of the  $2^3S$  level to the  $He^+$  current at 30 eV, we obtained accurate values for the effective well depth. The effective well depth found from the helium experiment is 30% lower than the peak well depth determined from electron retarding. It is found that the effective well depth for the data of Fig. 1 is 0.16 V.

Figure 2 is a plot of the cross section at 0.16 eV above the threshold vs vibrational quantum number. The data are taken from Fig. 1 and are consistent with numerous other experimental runs. A probable error of a factor of 2 should be associated with the absolute cross section scale. The relative numbers are, however, much more accurate, probably within 30%.

The points of Fig. 2 indicate that vibrational excitation of the ground electronic state,  $X^3\Sigma_g^-$ , takes place up to at least  $v=4$  and probably up to  $v=9$ . At the position  $v=5$  the cross section is enhanced over that for  $v=4$  and a reasonable extrapolation of the curve. This can be attributed to the excitation of the state  ${}^1\Delta_g$  in the zeroth vibrational state. However, the possibility that the cross section for  $v=5$  of the  $X^3\Sigma_g^-$  state is enhanced cannot be completely excluded. Again, a rise in the cross section is seen around the level  $v=8$  which may be due to the excitation of the  ${}^1\Sigma_g^+$  state.

The upper limits of the cross section to the  ${}^1\Delta_g$  and  ${}^1\Sigma_g^+$  states at 0.16 eV above threshold ( $3 \times 10^{-20}$   $cm^2$  and  $1 \times 10^{-20}$   $cm^2$ , respectively) are two orders of magnitude below the corresponding typical cross sections for electronic excitation of atoms and molecules. The high-lying electronic levels of  $O_2$  have cross sections in the  $10^{-18}$   $cm^2$  range, as shown in Fig. 3. The low values of the cross sections to the two low-lying states of  $O_2$  are consistent with the results of other experiments. Thompson,<sup>12</sup> studied the electron energy distribution in an oxygen plasma and found that the mean cross section for dissociation through the Schumann-Runge continuum is at least an order of magnitude larger than the cross section for the lower states, for electrons of about 11 eV energy. Lassetre<sup>12</sup> finds no trace of the low-lying electronic states at electron energies in the 100-eV range.

In order to excite the two low-lying states by electron impact with ground state molecules ( ${}^3\Sigma_g^-$ ) one requires a change of multiplicity, angular momentum, and symmetry. Selection rules may prevent the cross section from reaching a normal value.<sup>13</sup>

### IV. INELASTIC PROCESSES ABOVE 4 eV

Figure 3 shows a plot of the trapped-electron current vs electron energy in the range from 4 to 12 eV. A

<sup>12</sup> J. B. Thompson, Proc. Roy. Soc. (London) **A262**, 503 (1961); E. N. Lassetre, Radiation Research Suppl. I, 530 (1959).

<sup>13</sup> G. H. Dunn, Phys. Rev. Letters **8**, 62 (1962).

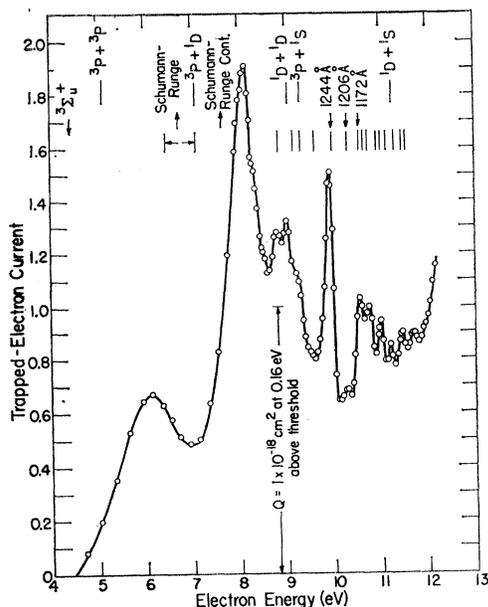


FIG. 3. Excitation spectrum of  $O_2$  above 4 eV. Peaks observed in optical absorption are indicated. The 1244 Å band is called the "longest" band, the 1206 Å band "second band," and the 1172 Å the "third band."

number of distinct peaks are evident and these can be correlated with optical absorption experiments.<sup>14</sup> The peaks and breaks observed in absorption by Watanabe, Inn, and Zelikoff<sup>15</sup> are indicated near the top of the figure. The position of these absorption peaks are, for the present comparison, in agreement with other investigations.<sup>16</sup> The dissociation limits are indicated by vertical lines and labeled with the spectroscopic terms of the dissociation products. The onset of the trapped-electron curve of Fig. 3 seems to occur near the position of the threshold of the  ${}^3\Sigma_u^+$  state and the next rise at the position of the threshold for the Schumann-Runge continuum, i.e., the  ${}^3\Sigma_u^-$  state. The assignment of the higher states is difficult and would be speculative.

## V. DISCUSSION

The existence of a stable negative ion in oxygen,  $O_2^-$ , is well established.<sup>17</sup> Thus, the  $O_2^-$  potential energy curve probably traverses many vibrational levels of the

<sup>14</sup> For a review, see G. L. Weissler, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956).

<sup>15</sup> K. Watanabe, E. C. Y. Inn, and M. Zelikoff, *J. Chem. Phys.* **21**, 1026 (1953).

<sup>16</sup> Y. Tanaka, *J. Chem. Phys.* **20**, 1728 (1952).

<sup>17</sup> Two recent values for the electron affinity of  $O_2$  are 0.58 eV obtained by R. K. Curran [*J. Chem. Phys.* **35**, 1849 (1961)] by electron impact on ozone, and 0.46 eV obtained from swarm experiments in  $O_2$  by A. V. Phelps and J. L. Pack [*Phys. Rev. Letters* **6**, 111 (1961) and *Bull. Am. Phys. Soc.* **7**, 131 (1962)].

$O_2$  system within the Franck-Condon region and one can expect vibrational excitation of  $O_2$  near the threshold of vibrational excitation, via the  $O_2^-$  system.<sup>18</sup> If the lifetime of the  $O_2^-$  system is short, the excitation function for the  $O_2^-$  system is broad and the onset of vibrational excitation of  $O_2$  will occur at the vibrational energy of the  $O_2$  system. If the lifetime of  $O_2^-$  is long,<sup>19</sup> the excitation function to the  $O_2^-$  system consists of sharp spikes at the position of the vibrational levels of  $O_2^-$ . In this case, the spacing of the vibrational onsets of  $O_2$  should correspond to the spacing of the  $O_2^-$  vibrational levels. Since the spacing of the vibrational levels of the  $O_2^-$  molecule is probably very close to the spacing of the  $O_2$  ground state,<sup>20</sup> we cannot experimentally distinguish between these two possibilities, nor can we exclude the possibility that direct excitation of vibrational levels is involved.

When one attempts to compare the present vibrational cross sections with those obtained from swarm experiments, one has to realize that swarm experiments measure the total inelastic energy loss cross sections, i.e., that portion of the cross section to the temporary negative ion state which leads to vibrational excitation. At a fixed electron energy there are various channels of decay available for the temporary negative ion. Thus, if the incident electron energy is slightly above the state  $v=2$  of  $O_2$ , the temporary negative ion can decay to  $v=0, 1$ , and 2. The present experiment only measures the cross section resulting in the population of the  $v=2$  level because the electrons resulting from a decay of the compound system to  $v=0$  and  $v=1$  are too energetic to be confined in the trap. In fact, a preliminary estimate by Phelps from swarm experiments shows that the inelastic cross section at an average energy of about 0.3 eV is an order of magnitude larger than shown in Fig. 2. The small cross section found for the low-lying electronic levels is consistent with swarm experiments.

## ACKNOWLEDGMENTS

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<sup>18</sup> Formation of stable  $O_2^-$  ions by electron impact on  $O_2$  can be observed only when a third body is present to carry off the excess energy; thus electron beam experiments at high pressure show the formation of  $O_2^-$  [G. J. Schulz, *Bull. Am. Phys. Soc.* **6**, 387 (1961)].

<sup>19</sup> D. C. Conway postulates a lifetime of  $1 \times 10^{-9}$  sec for the  $O_2^-$  system [*Bull. Am. Phys. Soc.* **7**, 131 (1962)].

<sup>20</sup> D. C. Conway (unpublished) finds the vibrational energy difference 1-0 for the  ${}^4\Sigma_g^-$  state of  $O_2^-$  to be 0.206 eV and for the  ${}^2\Pi_g$  state of  $O_2^-$ , 0.172 eV; this compares with a value of 0.196 eV for the ground state of  $O_2$ .