Low-Energy-Electron Attachment to Oxygen Clusters Produced by Nozzle Expansion

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Electron attachment to O_2 clusters gives two homologous series, $(O_2)_n^-$ and $(O_2)_nO^-$. Measured relative attachment-cross-section functions show significant differences, i.e., $(O_2)_nO^-$ ions show a similar behavior to O^- from O_2 (a single peak at ~ 7 eV), whereas $(O_2)_n^-$ ions show an additional peak at ~ 0 eV. The latter result explains the large thermal-electron attachment rates observed in high-pressure and low-temperature swarm experiments.

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Low-energy-electron attachment (< 20 eV) to the oxygen molecule in the gas phase has been the subject of intensive study in the past twenty years.[1-3] Reactions involving molecular oxygen and its anion are of importance in understanding air chemistry.[4] Dissociative attachment to O_2 is produced in the energy range 4.4 to 10 eV via

$$O_2(X\,^3\Sigma_g^-) + e \rightarrow O_2^{-*}(^2\Pi_u) \rightarrow O^-(^2P) + O(^3P). \quad (1)$$

The cross section for this process shows a single structureless peak at ~ 7 eV, suggesting that only a single repulsive state is responsible for the occurrence of this reaction. Nondissociative attachment to O_2 (which has a positive electron affinity of 0.440 ± 0.008 eV[4]) occurs by a resonance process,

$$O_2(X\,^3\Sigma_g^-; v=0) + e \rightarrow O_2^{-*}(X\,^2\Pi_g; v' \geq 4). \quad (2)$$

The molecular anion so formed is unstable with respect to autodetachment and has a predicted lifetime of $\sim 10^{-10}$ s,[5] unless it can be stabilized collisionally in a high-pressure environment. A two-step mechanism was suggested by Bloch and Bradbury[6] and later modified[7] and includes reaction (2) and

$$O_2^{-*}(X\,^2\Pi_g; v' \geq 4) + M \rightarrow O_2^-(X\,^2\Pi_g; v' < 4) + M + \text{energy}. \quad (3)$$

According to Spence and Schulz[8] and Mc Corkle, Christophorou, and Anderson[9] the "effective" cross section for this "three-body attachment" shows pronounced structure with energy. The peaks of this structure occur at the position of the vibrational levels of the O_2^- system serving as the intermediate product in the two-stage process (2) and (3).

Recent studies, however, which investigated the pressure and temperature dependence of attachment rates have demonstrated that attachment in pure O_2 and some O_2-M (where M denotes some other molecule) systems cannot be explained solely by the Bloch-Bradbury mechanism but that also attachment to van der Waals molecules has to be involved.[3,10-12] Although the density of van der Waals molecules in those experiments is much smaller than that of O_2 molecules, attachment to van der Waals molecules was thought to be much larger because of an assumed reduction in the effective resonance energy [0.076 eV for $O_2^-(v'=4)$ with respect to $O_2(v=0)$[11]]. The idea of electron attachment to oxygen dimers has been suggested and discussed earlier[8,13-15]; however, no direct (crossed-beam, single-collision) investigation of electron attachment to oxygen clusters exists. In this Letter we report the first direct study of electron attachment as a function of electron energy (~ 0 to 30 eV) to O_2 clusters. The clusters are formed by nozzle expansion and the attachment is studied in a crossed-molecular-beam, electron-impact–ionization, mass-spectrometer system under single-collision conditions.

The molecular-beam, electron-impact, mass-spectrometer system has been described previously.[16] Neutral clusters are formed by the expansion of up to 6 bars of O_2 through a 10-μm nozzle into vacuum. The stagnation-gas and nozzle temperature is variable (down to liquid-nitrogen temperature) and is kept constant during the experiment (typically $-140\,^\circ$C). The electron beam is guided by a weak magnetic field (~ 400 G) and has an energy spread of ~ 0.5 eV.[16]

The ions produced are extracted by a weak extraction field, whose possible influence on (i) the electron energy, (ii) the ionization (and presently attachment) process, and (iii) the measured cross section has been discussed previously.[16,17] The energy scale was calibrated with known cross-section curves of anions in O_2, CO_2, and SF_6. The extracted anions are analyzed in a double-focusing sector-field mass spectrometer with improved transmission characteristics.[16]

Two homologous series [$(O_2)_n^-$ and $(O_2)_nO^-$ with n up to 15] were observed by electron attachment to the neutral-oxygen-cluster beam. No effort was made to observe larger homologs. We have measured the relative attachment cross sections for some cluster anions and find significant differences from the known cross-section curve of O^- produced by dissociative at-

tachment to O_2. Figures 1(a)–1(d) show the measured electron energy dependence for the production of the O_2^-, $(O_2)O^-$, $(O_2)_2^-$, $(O_2)_4O^-$, and $(O_2)_{10}^-$ anions. Also shown in these figures for comparison and calibration purposes is the measured attachment-cross-section function for the production of O^- from O_2. The peak position and shape of the O^- from O_2 curve are in good agreement with previous high-precision determinations, i.e., a single structureless peak in the energy range 4.4 to 10 eV.[5,18]

Among the negative ions observed, those comprised of $(O_2)_nO^-$ appear at the same electron energies as O^- from O_2. Moreover, it can be seen that the peak cross section for $(O_2)O^-$ seems to be shifted slightly to higher energies as compared to O^- from O_2, and a small second peak beginning at ~ 13 eV is discernible in Fig. 1(d). Peak shifts upon solvation, although to lower energy, have been observed previously for $(CO_2)_n^-$, $(CO_2)_nO^-$,

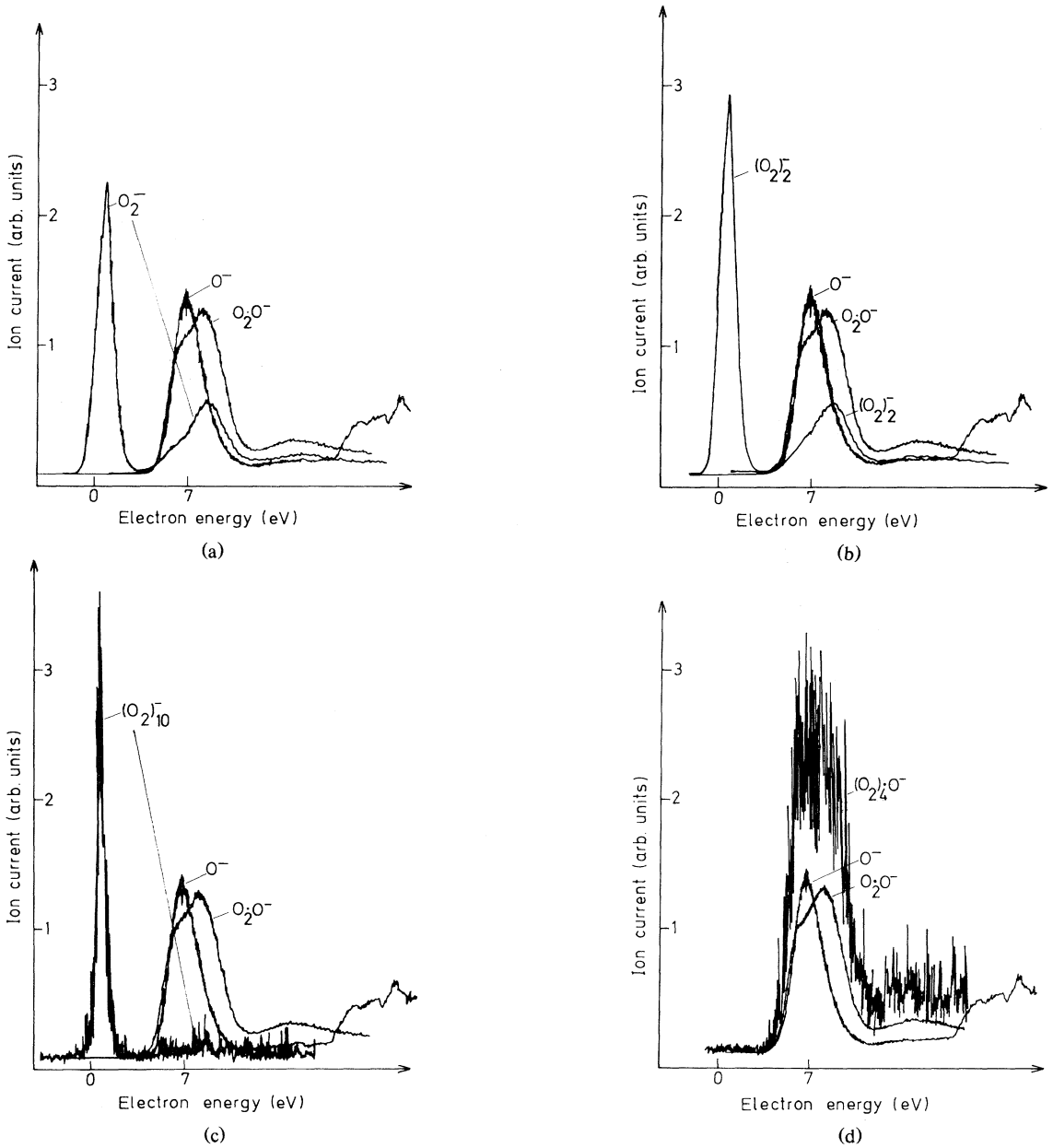

FIG. 1. (a)–(d) Anion signals produced by electron attachment to O_2 clusters as a function of electron energy. The cluster beam was produced by expansion of the O_2 gas under 5.6 bars and $-140\,^\circ$C. Also shown is the energy dependence of O^- produced via dissociative attachment to O_2. This curve (and also the anion curves of CO_2 and SF_6) is used to calibrate the energy scale with the help of the well-known peak parameters (Ref. 5).

and $(N_2O)_nO^-$ ions.[15,17,19-22] On the other hand, Sanche[23] reports a similar shift to higher energy and an additional hump at ~ 13 eV for dissociative attachment in electron scattering from condensed O_2. This second peak has been ascribed to the decay of another repulsive O_2^- state.[23] Nevertheless, the similar shape of attachment cross sections between these cluster anions and O^- suggests a production scheme starting with a dissociative attachment,

$$(O_2)_x + e \rightarrow (O_2)_{x-1}O^- + O, \quad (4)$$

followed by subsequent isomerization,

$$(O_2)_{x-1}O^- \rightarrow (O_2)_{x-2} \cdot (O_2)O^-, \quad (5)$$

leading to a boil off of one or more neutrals to release the produced heat of isomerization,

$$(O_2)_{x-2} \cdot (O_2)O^- \rightarrow (O_2)_{x-2-y} \cdot (O_2)O^- + y(O_2). \quad (6)$$

This production scheme, i.e., the neutral precursor being a heavier species than the anion, is confirmed by the observed dependence of ion intensities on stagnation pressure [e.g., the $(O_2)O^-$ ion signal peaks at much higher stagnation-gas pressures than that of the O_2^- and $(O_2)_2^-$ ions[24] (see Fig. 2)] and similar results for CO_2 clusters.[21]

We also observe a series of negative ions of the form $(O_2)_n^-$. The development of the relative attachment-cross-section curve as a function of cluster size is illustrated in Figs. 1(a)–1(c). It can be seen that these ions have, in addition to a slightly shifted peak at ~ 7 eV as compared to O^- from O_2, an additional peak close to zero electron energy. No anions have been observed previously in electron-O_2 crossed-beam experiments under single-collision conditions at this low electron energy. Moreover, it can be seen that the ratio of the peak at ~ 7 eV to the one close to 0 eV changes drastically between the O_2^- and the $(O_2)_{10}^-$; i.e., the larger cluster anions clearly have their maximum production probability close to zero electron energy. In addition, the FWHM of the zero-energy peak for $(O_2)_{10}^-$ is much smaller than that for the smaller clusters. It should be noted, however, that because of discrimination effects for ions with excess kinetic energy (and this could be the case for those ions produced at ~ 7 eV) and because of changes in the electron current close to zero electron energy (below ~ 2 eV it is very difficult to control the electron-beam properties) the presently observed peak ratios at ~ 0 and ~ 7 eV and the change in the FWHM only give a qualitative picture during the course of change from the monomer to the dekamer.

From additional experiments[24] and in accordance with similar measurements with CO_2 clusters[21] it may be concluded that, e.g., the O_2^- ions produced with electrons of ~ 7 eV have a larger neutral precursor than the ones produced with electrons close to 0 eV.

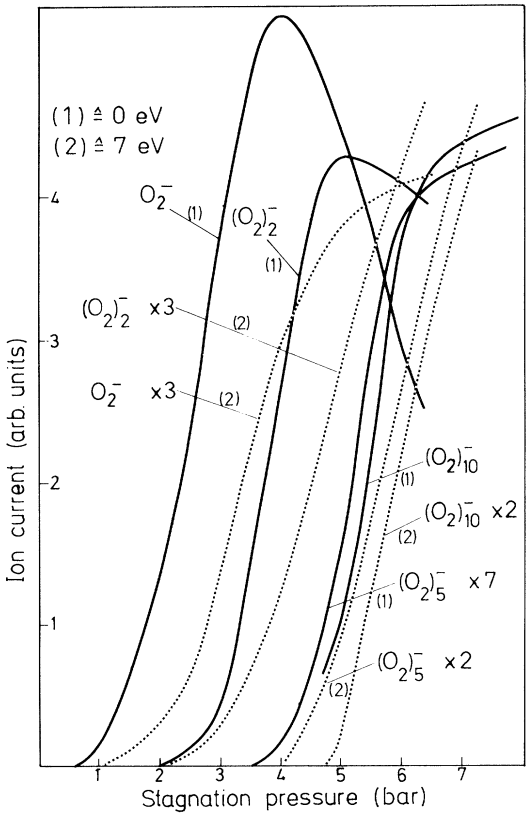

FIG. 2. Negative-ion signal for $(O_2)_n$ anions (produced via electron attachment to an O_2-cluster beam) for two different electron energies (~ 0 and ~ 7 eV, respectively) as a function of stagnation-gas pressure.

Moreover, the strong decrease of the peak at ~ 7 eV for $(O_2)_{10}^-$ is thought to be at least partly due to the fact that in the present experiments the distribution of the neutral clusters decreases very rapidly with cluster size and thus there are not enough neutral clusters with $n > 10$ available to populate the peak of the $(O_2)_{10}^-$ ions at ~ 7 eV. The observed decrease of the FWHM of the peak at ~ 0 eV indicates that electron attachment proceeds for larger clusters via a negative-ion resonance state, possibly a nuclear excited Feshbach resonance. This, however, would open the possibility for the existence of a long-lived parent anion without fragmentation before detection[25] of the ions. Such a behavior is known for large polyatomic molecules,[5] and it is postulated that the process also becomes operative in the present case.

Finally, the present observations clearly show that thermal electrons attach with high probability to oxygen clusters and this fact corroborates conclusions drawn from previously observed changes of attachment rate constants at low temperature and high pressures in high-pressure swarm experiments.[3,10-12] Moreover, with the help of the present results it is

possible to interpret (i) the gradual shift of the effective attachment cross section (reported by Mc Corkle, Christophorou, and Anderson[9]) toward lower energies with increasing gas density and (ii) the increase of magnitude with increasing gas density as evidence for the presence of clusters in these experiments.

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