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Vibrationally Resolved Electron Attachment to Oxygen Clusters

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Highly monochromatized electrons (with 30 meV FWHM) are used in a crossed beam experiment to investigate electron attachment to oxygen clusters $(O_2)_n$ at electron energies from approximately 0 to 2 eV. At energies close to zero, the attachment cross section for the reaction $(O_2)_n + e \rightarrow O_2^-$ rises strongly with decreasing electron energy compatible with s-wave electron capture to $(O_2)_n$. Peaks in the attachment cross section present at higher energies can be ascribed to vibrational levels of the oxygen anion. The vibrational spacings observed can be quantitatively accounted for by model calculations. [S0031-9007(96)01481-0]

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Few atomic collision processes have been investigated so thoroughly as those involving the electron and oxygen molecule, including intensive studies on electron attachment [1,2]. One of the reasons for this is that reactions involving molecular oxygen and its anions are of importance in understanding atmospheric chemistry [3]. Electron attachment to a single ground state oxygen molecule proceeds in the energy range from 4.4 to 10 eV via a dissociative channel, whereas, at low energies (below 1 eV), attachment to O_2 (which has a positive adiabatic electron affinity of EA $= 0.440 \pm 0.008$ eV [4]) results in a nondissociative resonance process [5,6]

$$O_2(X^3\Sigma_g^-; v = 0) + e \rightarrow O_2^{-*}(X\,^2\Pi_g; v' \geq 4). \quad (1)$$

Because the bond length of the neutral molecule is much smaller than for the anion [7] and because O_2 has a positive EA (see Fig. 1), the incoming electron cannot induce a Franck-Condon transition to the ground state of the anion. Instead, only vertical transitions to the fourth and higher vibrational levels of the anion are possible, the fourth vibrational level lying about 90 meV about the first vibrational level of the neutral [8]. The molecular anion formed via reaction (1) is unstable with a predicted [9] lifetime towards autodetachment of about 10^{-10} s. In a high pressure environment this anion can be stabilized collisionally to a vibrational level $v' < 4$ which lies below the $v = 0$ level of the neutral [see Fig. 1(a)], thereby making autodetachment impossible. According to Spence and Schulz [5] and McCorkle, Christophorou and Anderson [6], the "effective" cross section for this "three-body attachment" process (proceeding via the low-lying $^2\Pi_g$ compound state) shows pronounced structure with peak energies coinciding with the positions of the vibrational states of the O_2^- compound state with $v' \geq 4$ (see also Ref. [10]).

Recently, electron attachment to oxygen clusters was studied in crossed beam experiments showing at low energy a broad "zero energy" peak for the production of O_2^- and higher homologues, i.e., the stoichiometric $(O_2)_n^-$ anions [11,12] (the production of nonstoichiometric cluster anions was found to closely follow the energy dependence of the O^- production from the monomer). The position of this zero energy resonance was reported in the earlier measurements (using electron beams with an energy distribution of 0.5 eV FWHM) to lie close to 0 eV [11], whereas, in the later experiments, using an electron monochromator with a 0.2 eV FWHM, the maximum was found to lie at about 0.7 eV [12] (it is conceivable that this difference could be due to a distinctly smaller average cluster size in the later experiment, see below).

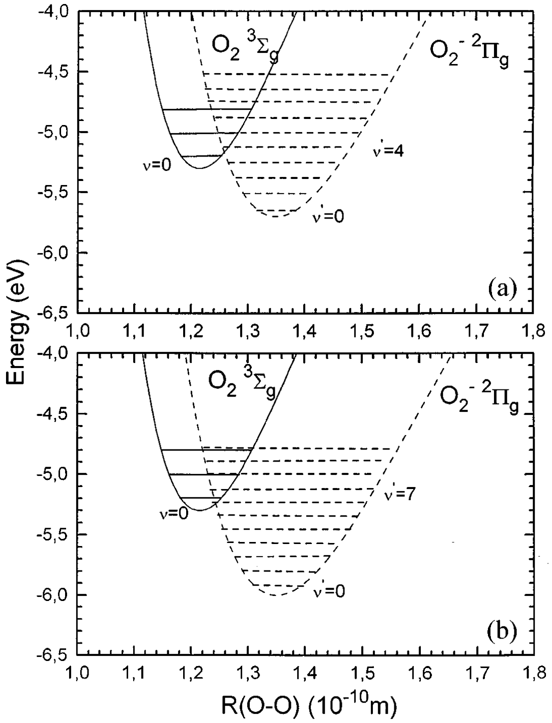

FIG. 1. (a) Approximate potential energy curves for O_2 and O_2^- after Spence and Schulz [5]. The $v' = 4$ state is located 0.091 eV above the $v = 0$ state [8]. (b) Hypothetical potential energy curves (see text for details of the applied shift between the two curves) for O_2 and O_2 solvated in an oxygen cluster. Note that the $v' = 7$ anion state is located in this hypothetical drawing approximately 80 meV above the $v = 0$ neutral state in accordance with the present experimental results.

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As no anions have been observed previously in electron/O_2 crossed beam experiments under single collision conditions at these low energies, the question remained (besides the observed discrepancy in the peak position): What is the exact attachment mechanism leading to the production of these ions at thermal energies?—An attachment reaction of importance in low temperature and high pressure swarm experiments [2].

In this Letter we report the results of a crossed electron/oxygen cluster beam study using a recently developed high resolution electron monochromator with a possible FWHM energy spread of as low as about 5 meV [13,14]. It is thus possible for the first time to resolve vibrational structure in electron attachment cross sections of clusters. Based on a theoretical analysis of (i) the cross section dependence on electron energy and (ii) the vibrational structure, it is possible to elucidate the attachment mechanism responsible for the specific energy dependence observed, i.e., involving, at very low electron energies, nonadiabatic s-wave capture of the incoming electron and, at energies above about 80 meV, Franck-Condon governed transitions to specific vibrational levels of a single oxygen molecule within the target cluster, in both cases followed by evaporative cooling.

The molecular-beam source, electron-impact ion source, and quadrupole mass spectrometer system have been described previously [13–15]. Neutral oxygen clusters $(O_2)_n$ are formed by the expansion of up to 5 bars of oxygen through a 20 μm nozzle into vacuum. The stagnation gas and nozzle temperature is variable and kept constant with a closed cycle cryostat during the experiment at a typical temperature of $-140\,^{\circ}\mathrm{C}$. The highly monochromatized electron beam is produced in a trochoidal monochromator especially designed [13,14] to achieve high resolution (in the present case using 30 meV FWHM, thus giving electron currents of 30 nA which are large enough to allow the study of electron capture reactions close to 0 eV). The anions produced in the collision region are extracted on line to the direction of the neutral cluster beam by a weak extraction field thus minimizing artifacts in the measured attachment cross section functions [16]. The zero energy position of the energy scale was calibrated and checked with the known cross section curves of anions of CCl_4 and SF_6 [14].

As in previous studies, two homologous anion series are observed by electron attachment to the neutral oxygen cluster beam. Figure 2 (full line) shows the measured relative attachment cross section function for the production of O_2^- and $(O_2)_2^-$ in the low energy regime produced via reaction

$$(O_2)_n + e \rightarrow (O_2)_m^- + \text{neutral products}. \qquad (2)$$

Measured cross sections exhibit the same characteristic behavior for all of these $(O_2)_m^-$ ions, i.e., the cross section is largest at about zero energy and then strongly decreases with increasing energy. Moreover, the decreasing cross section is structured by additional peaks whose maxima appear to lie (within the experimental error bar of ±10 meV) in all cases at the same energy, i.e., for the O_2^- ion shown in Fig. 2 the distance between the zero energy and the first additional peak is 82 meV, to the next peak 193 meV, and to the final peak still discernible at 299 eV, respectively. On average, the first additional peak lies at an electron energy of about 80 meV, whereas the average spacing between the next two peaks is approximately 113 meV and 109 meV, respectively. In the following, we will first discuss the nature of the first peak and then proceed to the interpretation of the structures.

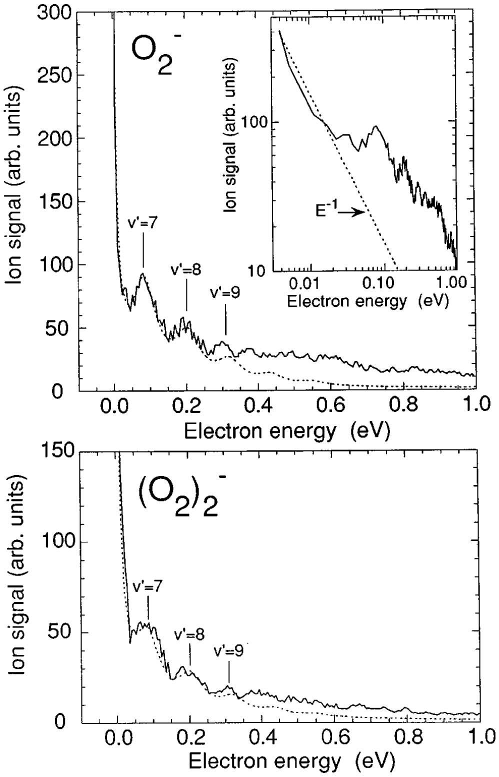

FIG. 2. Measured O_2^- (full line, upper panel) and $(O_2)_2^-$ (full line, lower panel) anion signal produced by electron attachment to a $(O_2)_n$ cluster beam as a function of corrected electron energy (electron current: 30 nA; energy resolution: 30 meV FWHM; guiding magnetic field: 50 G; ion extraction field: 100 meV/cm; stagnation pressure: 4.7 bars; stagnation temperature: $-138\,^{\circ}\mathrm{C}$). Also shown (broken line) is the calculated cross section behavior (see text). Inset: Measured O_2^- ion current versus corrected electron energy on a log-log scale. Dashed line indicates the E^{-1} dependence predicted by s-wave scattering theory.

The inset in Fig. 2 gives a log-log plot of the measured O_2^- ion current versus electron energy. It can be seen that the anion current decreases strongly with increasing energy before the appearance of the additional structures at approximately 30 meV. This strong decrease is compatible with the energy dependence predicted by quantum theory [17] for s-wave scattering (i.e., an E^{-1} dependence), and such a strong decrease has been observed for several molecules in this low energy region [9,13]. Thus we conclude that the present observation indicates that s-wave electron capture is also a likely mechanism in the electron attachment to oxygen clusters. After the initial s-wave capture of the electron by the entire $(O_2)_n$ cluster, subsequent inelastic scattering processes (energy losses to phonons) reduce the electron energy below the vacuum level and lead, via monomer evaporation, to the final reaction product observed, i.e., O_2^- (and higher homologues). It is interesting to note that a theoretical description of electron capture to $(CO_2)_n$ clusters [18] also gives a strong decrease with increasing energy in this very low energy region.

Peaks at higher electron energies are attributed to the attachment of an incoming electron to a single oxygen molecule within the target cluster via a direct Franck-Condon transition from the ground vibrational state $v = 0$ to a vibrational excited state v' of the ensuing anions (see lower part of Fig. 1). Subsequent collisional stabilization [19] of this anion within the cluster environment to a vibrational state below $v' = 4$ gives a stable O_2^-. The energy thus released leads to the evaporation of neutral oxygen molecules (the heat of condensation of O_2 with 1.63 kcal/mole [20] being the order of magnitude in energy which can be disposed in a single evaporation step). Depending on the amount of energy released (which depends on the v' state reached, see below) and on the size of the neutral precursor, this may lead to the production of naked O_2^- ions or to higher homologues such as O_4^-, O_6^-, etc.

Identification of the vibrational states populated in the anion can be done in two ways. Despite an absolute error margin of ±10 meV in the energy position of the peaks, the relative error for the vibrational spacings determined is much smaller, amounting to about ±5 meV. This gives a value of about 118 meV as an upper limit of the spacings which is certainly smaller than the known spacing between the $v' = 4$ and $v' = 5$ state of 125 meV [21]. From the table of the slowly decreasing spacings with increasing v' (given in Ref. [21] for the monomer), the peak present at 80 meV thus has to be either $v' = 7$ (as indicated in Fig. 1) or a higher state, assuming similar spacings in the monomer and solvated anion.

A similar result is obtained from the calculation of the downward shift of the anion potential in the cluster environment due to polarization forces (see [22]). To this end, we assume that the excess electron is localized initially on a specific molecule within the cluster. This is a good approximation, because the cluster is only weakly bound by van der Waals forces, and the distance between the molecules is large. Thus delocalization of the excess electron only becomes important later, when strongly bound dimer or trimer anions are formed via intracluster reactions. The electric field of the negative charge then polarizes the other molecules of the cluster. The corresponding energy V_p has been calculated using the model given in Ref. [23] and strongly depends on the position r of the molecular anion in the cluster, and on the size and the structure of the cluster. A constant temperature molecular dynamics calculation ($T = 20$ K) yields the distributions f for V_p, which are shown for the three cluster sizes 10, 15, and 20 in Fig. 3 as a function of the adiabatic electron affinity (defined as the sum of the polarization energy V_p and the adiabatic electron affinity of the monomer).

Two important conclusion can be drawn from the results shown in Fig. 3. At a typical cluster temperature of 20 K there exists only a small range of possible polarization energies independent of the precursor sizes probed. Thus the shift induced by this polarization energy is well defined, and the value of 0.8 eV for the total adiabatic electron affinity (thereby assuming that the initial neutral precursor has an approximate size of 15 to 20 molecules, which is also compatible with the energy necessary to evaporate 14 of those molecules) is close to the value used for constructing the hypothetical potential curves shown in the lower part of Fig. 1. This leads to a situation where $v' = 7$ is the first vibrational state accessible via a vertical Franck-Condon transition by electron attachment in accordance with the conclusion drawn above from a comparison between the measured and the known vibration spacings. Moreover, a further confirmation of this identification comes from a calculation where we have modeled the energy dependence of the attachment cross section (see broken line in Fig. 2), adding to the s-wave scattering component calculated contributions resulting from the respective Franck-Condon overlap

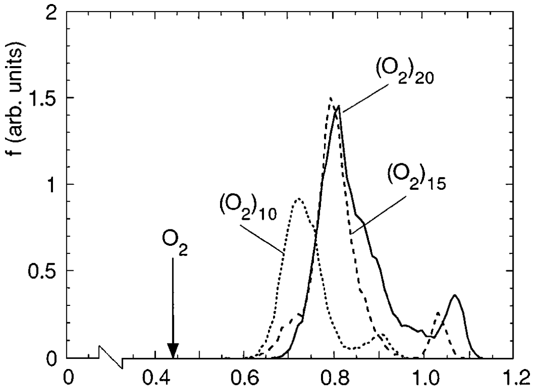

FIG. 3. Calculated distribution function f (for the various possible cluster structures and various positions of the solvated O_2^- ion in the cluster, respectively) of the adiabatic electron affinity EA$_a$, taking into account the polarization energy V_p in the nascent cluster anion for neutral precursor sizes of 10, 15, and 20 oxygen molecules at 20 K cluster temperature. The arrow designated O_2 indicates the electron affinity of the single molecule. The first (major) peak around 0.8 eV is due to structures where the anion is assumed to reside at the surface of the cluster, and the second (minor) peak around 1 eV is due to anions at the center.

integrals. Note that the peaks in Fig. 2 for $v' = 7, 8, 9$ have a slightly larger width than the peak in Fig. 3 at 0.8 eV. The excellent agreement between the experimental shape and the theoretical prediction (up to the fourth peak, see Fig. 2; the higher order transitions are possibly contaminated in the experiment by additional reaction channels above 0.4 eV, e.g., p-wave capture) not only confirms the vertical shift when going in Fig. 1 from the monomer to the cluster, but also the horizontal position of the hypothetical potential energy curve, i.e., using for the anion in the cluster case the same bond distance of 1.34×10^{-10} m as in the monomer case [4].

In conclusion, we report, for the first time, vibrationally resolved electron/cluster attachment spectra measured in a crossed beam arrangement under single collision conditions. This is possible using a high performance monochromator in conjunction with a cryostat cooled cluster source and a high efficiency detection system. The measured electron energy dependence demonstrates, on the one hand, that, at energies close to zero, the incoming electron is very likely captured by the entire cluster via s-wave scattering, whereas peaks at higher energy can be quantitatively ascribed to the vertical attachment of the incoming electron at one cluster molecule, thus leading to the Franck-Condon transition from the vibrational ground state of the neutral to the excited vibrational states in the anion with $v' \geq 7$.

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