Dissociative Attachment in Electron Scattering from Condensed O_2 and CO

L. Sanche
Medical Research Council Group on Radiation Sciences, Faculté de Médecine, Université de Sherbrooke, Sherbrooke, Québec J1H 5N4, Canada

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The formation of O^- and C^- ions via dissociative attachment in electron scattering from O_2 and CO condensed on a polycrystalline platinum surface is reported. Below 15-eV impact energy, O^- from O_2 arises essentially from the repulsive $^2\Pi_u$ state of O_2^-, whereas in CO, C^- and O^- appear to be emitted from higher-energy repulsive states of CO^- with yields much different from those found for the isolated molecule.

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The formation of negative ions by electron impact is a process of fundamental and practical importance in many areas of physics and chemistry.[1,2] There exist essentially two mechanisms by which isolated molecules[1] may dissociate and form negative ions by colliding with electrons: polar dissociation and dissociative attachment. For a diatomic molecule AB these processes may be represented, respectively, by the equations

$$e + AB \rightarrow AB^* + e \rightarrow A^+ + B^- + e, \quad (1)$$

$$e + AB \rightarrow AB^- \rightarrow A + B^-. \quad (2)$$

The first reaction proceeds via an excited state AB^* and the second via a transient anion AB^-. Reaction (2) has been intensively investigated in a large number of isolated (gas-phase) electron-molecule systems.[1,3-6] This Letter reports the first observation of the process for molecules condensed (i.e., physisorbed) on a metal surface.

The apparatus consists of an electron gun, a refrigerated target, and a mass spectrometer housed in an UHV system reaching pressures below 5×10^{-11} Torr. Electrons are accelerated to an electrically isolated polycrystalline platinum ribbon press fitted on the cold end of a closed-cycle refrigerated cryostat. The angle of incidence is 20° from the surface. Condensed layers of O_2 and CO are grown on the ribbon and the film thickness estimated, within 50% accuracy, as previously described.[7] Negative ions produced by electron impact on the condensed film are measured as a function of electron energy by a quadrupole mass spectrometer equipped with ion lenses and positioned at 70° from the film surface. In order to prevent stray electrons from reaching the mass spectrometer detector and to obtain reasonable electron densities down to about 0.4 eV, the electron beam is collimated by an axial magnetic field of 15 G. The energy spread of the electron beam was 0.3 eV. Its energy was calibrated within ±0.4 eV with respect to the vacuum level by measuring the onset of electron transmission through the films and by comparing the energy of the structure in the transmission spectra with those obtained at high resolution.[8] The target ribbon was cleaned by argon bombardment and heated at elevated temperatures. After cooling, the target temperature could be monitored by a gold-iron thermocouple located behind the platinum ribbon. The data were recorded with incident electron currents of about 10^{-8} A, a target temperature of 21 K, and film thickness varying from submonolayer coverage to about 75 Å.

O^- and C^- ion currents measured as a function of electron energy are shown in Figs. 1 and 2 for electrons incident on six-"monolayer"-thick films of O_2 and CO, respectively. The *intensity* in counts/sec is obtained *by multiplying the left-hand scale by the factor which appears near each recording.* The data were obtained with the ion lens adjusted to transmit principally low-energy (0–2 eV) ions. The bottom curve in Fig. 1 represents the energy dependence of the cross section for producing O^- by electron impact on O_2 gas.[9] The strong peak in the cross section at 6.5 eV arises from the dissociative attachment reaction[4]

$$e + O_2(^3\Sigma_g^-) \rightarrow O_2^-(^2\Pi_u) \rightarrow O^-(^2P) + O(^3P). \quad (3)$$

A similar peak occurs at 6.6 eV in the present experiment with an onset at 4.6 eV which compares with the value of 4.4 eV in the gas found by Schulz.[3] When normalized to the O^- intensity at 35 eV, the magnitude of the 6.6-eV peak arising from the solid surface appears to be *two orders of magnitude smaller than that in the gas phase.* The onset of dipolar dissociation lies around 15 eV and compares with the gas-phase value[9] of 16 eV. Between 11 and 15 eV a weak "hump" appears at 13.0

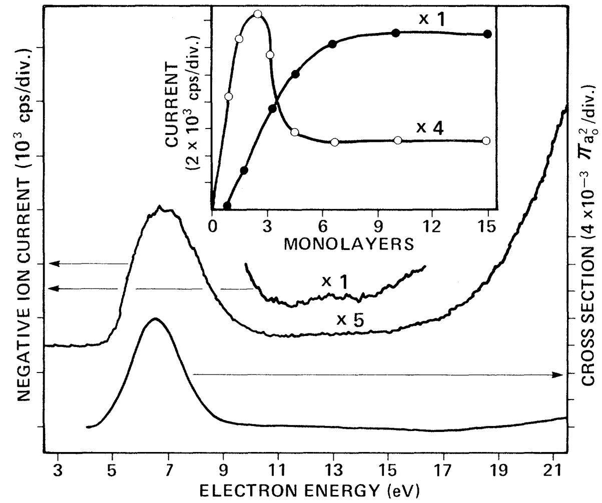

FIG. 1. Energy dependence of the O^- yields produced by electron impact on a six-"monolayer"-thick film of condensed O_2 and on gaseous O_2 (bottom curve; from Ref. 9). The inset shows the film-thickness dependence of the O^- signal produced by 7-eV (full circles) and 21-eV (open circles) electrons. The intensity of the signal is obtained by multiplying the left scale by the factor which appears on top of the upper curves.

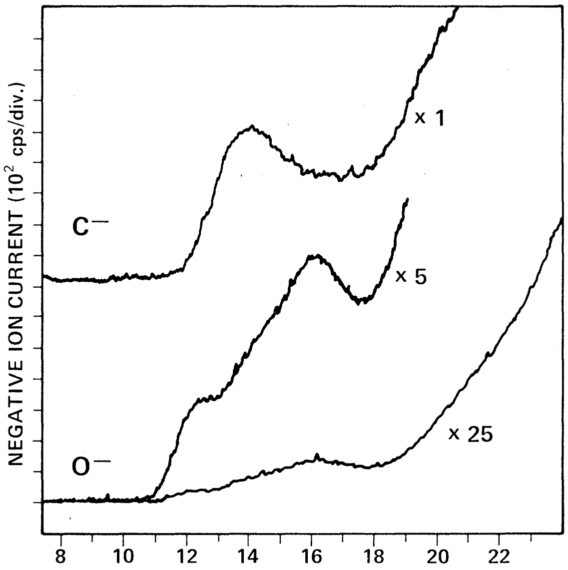

FIG. 2. Energy dependence of C^- and O^- yields produced by electron impact on a six-"monolayer"-thick film of condensed CO.

eV.

The behavior of the O^- intensity as a function of film thickness is shown in the inset of Fig. 1. The solid circles represent O^- ions arising from electron bombardment with 7-eV impact energy. Values for the open circles were recorded at incident energies of 21 eV where dipolar dissociation is usually the dominating process.[1] The horizontal scale represents the approximate number of monolayers in the film assuming layer by layer growth.

The energy dependence of O^- and C^- yields from the CO surface is different from that found in the gas phase[10] where dissociative attachment reactions lead to a sharp onset in O^- production at 9.65 eV followed by a maximum near 9.8 eV and a C^- signal with two maxima around 10.5 and 11 eV. Here, O^- production sets in at 10.6 eV and has maxima near 12 and 16 eV; the C^- signal is completely absent in the range 10–11.5 eV where data is available from the gas phase.[10] In the 12–16-eV region, however, C^- production from the solid exhibits a maximum near 14 eV. Its intensity is about an order of magnitude smaller than that of the O^- maximum at 16 eV. *This ratio is drastically different in free CO where the cross section for O^- formation at 9.8 eV*[10] *is 3 300 stronger than that for C^- production at 10.5 eV!* The O^- intensity in the 12–14-eV range is found to be two orders of magnitude smaller than that found in the 10–12-eV range for isolated CO, when normalized to the O^- intensity at 35-eV impact energy.

Back donation of an electron from the metal[11] to a dissociating molecule located at or near the surface of a multilayer insulating film is a very unlikely process. Thus, below the threshold for dipolar dissociation, the only plausible mechanism which can produce O^- and C^- ions appears to be dissociative attachment. Furthermore in condensed O_2, the negative ion state $^2\Pi_u$, which is known to lead to the 6.5-eV O^- peak in the gas,[1,3,4] has recently been observed to cause a strong enhancement of vibrational excitation in the 6–8-eV region.[12] The 6.6-eV peak in condensed O_2 (Fig. 1) is therefore ascribed to reaction (3). The small "hump" at 13 eV probably arises from the decay of another repulsive O_2^- state. In fact, the amplitude of this structure could be increased by tuning the ion lens at higher energy, thus indicating the presence of a different state.

In the condensed phase, transient anions occur at lower energies than in the gas, mainly because of the electronic polarization of the neighboring molecules.[12,13] However, in the dissociative attachment process only O^- ions which overcome this polarization force can escape the solid, so that only the higher-energy portion of the O^- distribution (produced by higher-energy electrons) is observed in vacuum. The two effects have a tendency to cancel each other and could account for the observation of O_2^- ($^2\Pi_u$) state at about the same energy in both phases. The delayed onset for O^- and C^- production in condensed CO can arise from a strong depletion of the reactions

$$\mathrm{CO}+e \to \mathrm{CO}^- \to \mathrm{O}^-(^2\mathrm{P})+\mathrm{C}(^3\mathrm{P}) \to \mathrm{O}(^3\mathrm{P})+\mathrm{C}^-(^4\mathrm{S}). \tag{4}$$

This depletion should increase the relative magnitude of other dissociative attachment reactions arising from CO^- potential-energy curves lying at higher energies.

More generally, the strong depletion of the dissociative attachment process relative to dipolar dissociation can be understood by considering the following sequence of steps leading to anion emergence into vacuum: (1) the initial electron capture at a particular molecular site leading to the formation of a transient negative ion; (2) the decay of the anion into the accessible channels including dissociative attachment; (3) the modification of the escaping ions as they recede from the solid. If we take Q_0 as the cross section for the formation of the initial transient anion (step 1), the cross section leading to dissociative attachment is given by[14]

$$Q_- = Q_0 \exp\left[-\int_{R_0}^{R'} \frac{\Gamma(R)\,dR}{\hbar v(R)}\right]$$

The exponential term represents the probability that in step 2 the anion will survive from an initial internuclear distance R_0 to a stabilization point R' beyond which the electron is bound to one of the detaching moieties. These latter move with a relative velocity of separation $v(R)$. Q_- is strongly dependent on the lifetime $\hbar/\Gamma(R)$ of the anion. This factor can therefore account partially for the large decrease in dissociative attachment signal arising from condensed O_2 and CO, since transient anions have so far been found to have a reduced lifetime in the condensed phase.[12,13] A quick estimate, under the assumption that the lifetime of an anion changes from 3×10^{-15} to 10^{-15} sec, shows that Q_- would be reduced by about three orders of magnitude if the stabilization time were taken as $\sim10^{-14}$ sec.

Further significant decrease in the negative-ion signal can occur via step 3, since escaping ions can lose their additional electron by interaction with neutrals forming the film. Cross sections for electron detachment range from $\sim10^{-15}$ to $\sim10^{-16}$ cm^2 for O^- scattering from CO at energies near 0 eV to about 5 eV, respectively.[15] In O^- scattering from O_2, the cross sections have an opposite trend starting below $\sim10^{-18}$ at 0 eV and increasing almost linearly up to the value of $\sim2\times10^{-16}$ cm^2 at 17 eV.[15] For the situation of interest here, this implies that the low-energy (1–3-eV)[1] O^- ions produced via the $^2\Pi_u$ state of O_2^- are likely to escape the film without a significant loss of electrons. Thus, the energy dependence of the O^- yield is expected to exhibit a similar behavior in both phases. In CO, however, the low-energy O^- ions (0–2 eV)[10] produced by the lowest-energy potential curve would react strongly with the surrounding matrix. It is therefore unlikely than an O^- ion arising from reaction (4) can escape the CO film without losing an electron. The extremely large cross section for electron detachment from O^- in CO could therefore qualitatively explain the delayed onset for O^- production reported in Fig. 2.

Finally, the result shown in the inset of Fig. 1 indicates that the dissociative attachment process does not seem to be influenced by the platinum surface, whereas the dipolar dissociation mechanism is enhanced at low coverages where escaping ions are more likely to arise from molecules physisorbed on the metal. This enhancement may be attributable to the screening or neutralization by metal electrons of the remaining positive ions, a process which is expected to increase the kinetic energy of the detaching anions and therefore decrease the relative probability of other competing processes to occur before stabilization of the negative charge on one of the detaching atoms.

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