Dissociative Attachment from Condensed O_2: Violation of the Selection Rule $\Sigma^- \leftrightarrow \Sigma^+$

R. Azria,[a] L. Parenteau, and L. Sanche
Medical Research Council Group in Radiation Sciences, Faculté de Médecine,
Université de Sherbrooke, Sherbrooke, Quebec, Canada J1H 5N4
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The formation of O^- ions via dissociative attachment in electron-stimulated desorption from condensed O_2 on a polycrystalline platinum surface is reported. The energy dependence of the O^- yield exhibits two peaks at 7 and 13 eV. The 7-eV peak arises from the $^2\Pi_u$ state of O_2^-, whereas the 13-eV peak is ascribed to two distinct resonance states, the $^2\Pi_u$ and the $^2\Sigma_g^+$ O_2^- states, from ion kinetic energy measurements. The $^2\Sigma_g^+$ O_2^- state is then accessible by attachment of an electron to the $X\,^3\Sigma_g^-$ O_2 target via a violation of the selection rule $\Sigma^- \leftrightarrow \Sigma^+$.

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The dissociative attachment (DA) process in gaseous O_2 has been intensively studied since the pioneering work of Tate and Smith[1] in 1932. Although 24 molecular O_2^- states can be formed from the interaction of the ground fragments $O(^3P)$ and $O(^2P)$, the cross section for O^- formation exhibits a single broad peak at 6.7 eV associated with the $^2\Pi_u$ O_2^- negative-ion state via the reaction[2,3]

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

In recent years, electron-stimulated desorption (ESD) of negative ions has been observed from a number of condensed (i.e., physisorbed) molecules[4] demonstrating the presence of a DA mechanism responsible for producing negative ions below the energy threshold of dipolar dissociation. For condensed O_2, Sanche[4] reported two structures in the O^- yield: one appearing as a peak at 6.6 eV associated with the $^2\Pi_u$ O_2^- resonant state and an another one around 13 eV appearing as a very weak "hump." This latter was tentatively attributed to another unspecified repulsive state of O_2^-, as its amplitude could be increased by tuning of the ion lens of the system to a higher pass energy. We report in this Letter a reinvestigation of ESD from condensed O_2, especially in the 13-eV range, which now includes O^--ion kinetic energy (KE) measurements. This advance in the technique allows us to associate the 13-eV peak to two different DA mechanisms, one of them occuring via the $^2\Sigma_g^+$ O_2^- state. It is the first example of a violated selection rule in a DA process.

The basic features of the apparatus have been described previously.[4] Briefly, it consists of an electron gun, a quadrupole mass spectrometer, and an electrically isolated polycrystalline platinum ribbon press fitted on the cold end of a closed-cycle refrigerated cryostat on which are grown condensed O_2 layers. These elements are housed in an UHV system reaching pressures below 5×10^{-11} Torr. The mass spectrometer is equipped with ion lenses followed by three grids of about 60% transparency. These grids serve to analyze the ion energies by the retarding-potential method. The apparatus can be operated in two modes: the ion-yield mode in which negative ions of a selected mass produced by electron impact on the condensed film are measured as a function of electron energy, and the ion-energy mode in which the negative-ion current at a selected mass is measured for a fixed electron energy as a function of the retarding potential. The first energy derivative of the curve thus obtained represents the energy distribution of the negative ions studied at the chosen incident electron energy. In the present experiment, the energy spread of the electron beam was 0.3 eV and its energy was calibrated within ±0.4 eV with respect to the vacuum level as previously described.[4] The overall energy resolution in the ion-energy mode was 0.5 eV and it was not possible to obtain an absolute scale for the ion KE. The film thickness was

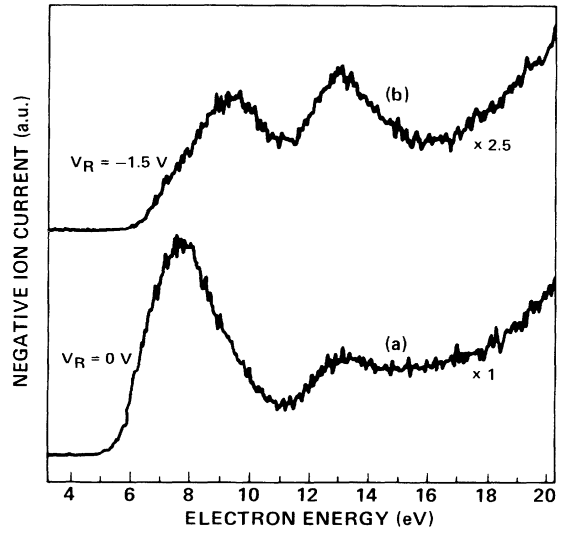

FIG. 1. (a) Energy dependence of the O^- yield produced by electron impact on a three-layer-thick film of condensed O_2. (b) Energy dependence of the O^- yield recorded with a retarding voltage of about 1.5 eV.

estimated within 50% accuracy by the gas-volume-expansion procedure previously described by Sanche.[5] The data were recorded with incident electron currents of about 10^{-9} Å, a target temperature of 21 K, and film thickness of about 3 layers.

The O^- ion current measured as a function of electron energy is shown in Fig. 1a. When compared to the results of Sanche, the structure at 13 eV now appears as a peak instead of a very weak hump. Also, the maximum of the first peak is slightly shifted toward higher energy. In fact, the Sanche data were recorded with the ion lenses adjusted to transmit principally low-energy ions, thus discriminating against higher-energy ones, which are present in the O^- yield as illustrated in Fig. 1(b). This figure represents the energy dependence of the O^- current recorded with a retarding voltage of about 1.5 eV applied to the middle grid of the energy analyzing device. We see clearly from this curve that the 13-eV peak is not affected in position by this retarding potential since it contains essentially high-energy ions. However, this is not the case for the first peak which has been artificially shifted to high energy by this cutoff. KE distributions of O^- ions at 5.7, 7.7, 12, and 13 eV incident energy are shown in Fig. 2. These curves indicate, first, that in the energy range of the 13-eV peak O^- ions arise from two distinct DA processes, one of them leading to O^- ions with about the same KE as those of the 7-eV peak and the other one with an average excess energy of 2.5 eV. Secondly, they indicate an ion-energy distribution much broader than that of the analyzing grids.

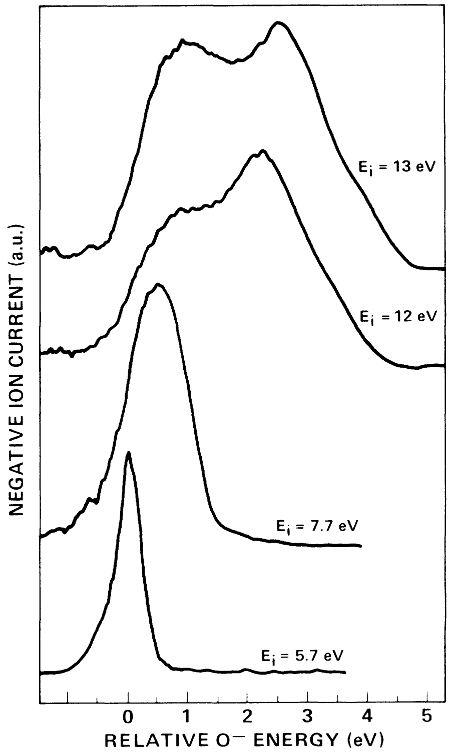

FIG. 2. Energy distribution of O^- ions at $E_i = 5.7$, 7.7, 12, and 13 eV. The ion energy is referred to the maximum in the energy distribution of O^- ions at $E_i = 5.7$ eV.

When we consider the DA reaction on a diatomic molecule, i.e.,

$$e + XY \rightarrow XY^{-*} \rightarrow X^- + Y^*,$$

the excess reaction energy E is given by

$$E = E_i - (\Delta + E_n - A),$$

where Δ is the dissociation energy of the neutral molecule, A the electron affinity of X, E_i the incident electron energy, and E_n the excitation energy of the neutral fragment. This excess energy is shared between the dissociating fragments as KE. From energy and momentum conservation, the KE of the negative-ion fragment is given by

$$E_r = (1 - \beta)[E_i - (D + E_n - A)],$$

where β is the ratio between the mass of the ion and the mass of the molecule. In the case of a homonuclear diatomic molecule β is $\frac{1}{2}$; then the curve representing the KE of the negative ions as a function of incident electron energy is a straight line with a slope $\frac{1}{2}$. This is, in fact, the case for O^- ions from gaseous oxygen in the whole energy range of the $^2\Pi_u$ resonance.[6] However, any observation other than a single peak in KE distributions at a given electron energy has to be associated with dissociating fragments in different electronic states. The situation is not so clear in the condensed phase. We see from Fig. 2 that as we go from $E_i = 5.7$ to 7.7 eV, the maximum in the KE distribution is only shifted by about 0.5 eV instead of the 1 eV expected. Concurrently, the width at half maximum of the energy distribution curve increases by almost a factor of 2.5. We attribute this broadening to multiple collisions (i.e., to electrons which have suffered single and multiple vibrational or electronic losses before attaching to O_2 to form the $^2\Pi_u$ state which dissociates to $O + O^-$). This is supported by Sanche and Michaud[7] who find that in the energy range of the $^2\Pi_u$ resonance in condensed O_2, vibrational excitation up to $v = 4$ and excitation of the $^1\Delta_g$ O_2 state is enhanced by orders of magnitude.

Similarly, for the 13-eV region, we ascribe the low-energy peak in the KE distribution to O^- ions formed via the $^2\Pi_u$ O_2^- resonance by electrons which have suffered energy losses through the excitation of the $A\,^3\Sigma_u^+$ and the $B\,^3\Sigma_u^-$ states and the Schumann-Runge continuum[8,9] of molecular oxygen. We associate the high-energy peak in the KE distribution around 13 eV to another repulsive O_2^- resonant state. Krauss and coworkers[10] have calculated the 24 electronic O_2^- states correlated to $O(^3P)$ and $O^-(^2P)$ fragments at infinite nuclear separation. They mentioned that among these only the $^2\Pi_g$, $^2\Pi_u$, $^{2,4}\Sigma_u^-$, and $^2\Sigma_g^+$ O_2^- states intersect the Franck-Condon region of the $v=0$ vibration of the neutral ground state. All these states, except the $^2\Sigma_g^+$, have been assigned to specific electron-scattering processes. Addition of a π_g electron to the lowest electronic configuration of O_2, i.e., $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2$) gives rise to the lowest shape resonance which decays[11] to vibrational excitation in the incident energy range 0-1.6 eV. The $^2\Pi_u$ $O_2{}^-$ state with configuration $\ldots 3\sigma_g^2 1\pi_u^3 1\pi_g^4$ is a valence-type Feshbach resonance, which is responsible for O^- formation around 7 eV. This resonance decays also into the $a\,^1\Delta_g$[7,12,13] and high vibrational levels of the $X\,^3\Sigma_g^-$ ground state[14] of O_2. The $^{2,4}\Sigma_u^-$ states are the two shape resonances with configuration $\ldots 3\sigma_g^2 1\pi_u^4 1\pi_g^2 3\sigma_u$ which contribute to large vibrational excitation of the $^3\Sigma_g^-$ O_2 ground state around 9 eV.[7,12] The $^2\Sigma_g^+$ $O_2{}^-$ state is a valence-type Feshbach resonance with configuration $\ldots 3\sigma_g 1\pi_u^4 1\pi_g^4$ which is not normally accessible by electron attachment to the $X\,^3\Sigma_g^-$ O_2 target because this would require a change in reflection symmetry[15] $(- \rightarrow +)$ during the process and therefore this resonance has not been observed in the gas phase.

DA processes appearing in the condensed phase and not in the gas phase must therefore be associated with isolated dimers or polymers existing in the condensed phase or with transitions forbidden in the gas phase, since transient anions have been so far found to have a reduced lifetime in the condensed phase compared to the gas phase thus giving a smaller cross section for negative-ion formation.[4,7] Because isolated dimers do not exist in pure condensed oxygen,[7,16] we postulate that the ESD of highly energetic O^- ions in the 13-eV energy range proceeds via a DA mechanism involving the $^2\Sigma_g^+$ $O_2{}^-$ resonance, the $(- \rightarrow +)$ selection rule being violated in the condensed phase because of the presence of the neighboring molecules.

The occurrence of forbidden electronic transitions is a well-known phenomena in photon absorption, in particular in the absorption spectra of oxygen at high pressures and in the liquid and solid states.[17] The present results indicate that similarly anion states forbidden by electron impact in the gas phase can be formed upon condensation. ESD thus provides a method by which resonances not observed in the gas phase can be detected. Further work is needed to understand fully the mechanism responsible for such transitions.

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