Mechanisms for O− electron stimulated desorption via dissociative attachment in condensed CO

R. Azria, L. Parenteau, and L. Sanche

Articles you may be interested in

Theory of electron stimulated desorption and dissociation of CO at transition metals
J. Chem. Phys. 117, 4489 (2002); 10.1063/1.1498474

Electron stimulated desorption via dissociative attachment in amorphous H2O
J. Chem. Phys. 94, 8570 (1991); 10.1063/1.460090

Dissociative attachment reactions in electron stimulated desorption from condensed O2 and O2doped rare gas matrices
J. Chem. Phys. 91, 2664 (1989); 10.1063/1.456976

Dynamics of dissociative attachment reactions in electron stimulated desorption: Cl− from condensed Cl2
J. Chem. Phys. 87, 2292 (1987); 10.1063/1.453160

Dissociative attachment in electronstimulated desorption from condensed NO and N2O
J. Vac. Sci. Technol. A 4, 1240 (1986); 10.1116/1.573406

Mechanisms for O⁻ electron stimulated desorption via dissociative attachment in condensed CO

R. Azria,[a] L. Parenteau, and L. Sanche

Canadian Medical Research Council Group in Radiation Sciences, Faculté de Médecine, Université de Sherbrooke, QC J1H 5N4, Canada

The formation of O⁻ ions via dissociative attachment (DA) in electron stimulated desorption from condensed CO is reported. The $^2\Pi$ states of CO⁻ previously observed in the gas phase and CO⁻ states with the forbidden symmetry Σ^- are involved below and above 13 eV, respectively, in the DA processes. Measurements of the kinetic energy of O⁻ ions indicate that they suffer post dissociation interactions with the neighboring CO molecules before leaving the solid.

I. INTRODUCTION

It is now well established that, below the energy threshold for dipolar dissociation, electron stimulated desorption (ESD) of negative ions from condensed molecules proceeds via dissociative attachment (DA).[1] This process constitutes a particular channel for the decay of transient anions, formed within molecular solids and near their surfaces, by the temporary capture of a low-energy electron at a molecular site. For a diatomic molecule AB, the DA mechanism is represented by the following reaction:

$$e^- + AB \rightarrow AB^{-*} \rightarrow A^- + B^*.$$
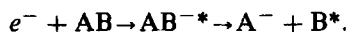
Since a given configuration of a transient anion AB⁻ appears at a well-defined energy, each peak in the electron-energy dependence of the A⁻ yield in gas-phase experiments identifies the energy of a particular AB⁻ state. In the condensed phase, such peaks (i.e., those in the anion ESD yields) are more numerous.[2–4] It has been found that this result could originate from two different mechanisms: the disappearance of the selection rule $\Sigma^- \leftarrow\!\!\!|\rightarrow \Sigma^+$ for electron attachment due to the change in the symmetry of the electron–molecule potential induced by condensation, and electronic excitation of condensed molecules by electrons prior to attachment at a molecular site.[3–5] The effect of multiple inelastic scattering, both vibrational and electronic, has also been observed on the anion kinetic-energy (KE) distributions recorded at a fixed electron energy. These distributions are usually strongly modified from those of the free-molecule experiments, exhibiting peak broadening and additional structures. They provide information on the electron energy degradation processes within the film and at its surface.[2,3]

To extend our present understanding of the microscopic sequence of steps leading to anion emergence in vacuum,[5] we have investigated O⁻ ESD from condensed CO. The electron-energy dependence of the O⁻ yield from condensed CO was previously reported by Sanche.[1] He noticed that the yield function was very different from that recorded in the gas phase[6] where two DA reactions leading to O⁻ formation are observed to produce a yield with a sharp onset at 9.62 eV followed by a maximum around 9.8 eV associated with

C(^3P) fragments and a hump in the region of 11 eV extending to 13 eV associated with C(^1D) fragments. The two resonant CO⁻ states involved in these reactions have been found from angular distributions analysis of O⁻ ions to have the $^2\Pi$ symmetry.[7]

In this paper, we report on the effect of the film thickness on the energy dependence of the O⁻ yield and on the KE distributions of O⁻ ions. In particular, we show that CO⁻ transient anions with configurations Σ^-, which are inaccessible in the gas phase from the CO ground state Σ^+, due to symmetry rules are involved in condensed state DA. We also find that post dissociation interaction (PDI) of stable O⁻ ions with CO molecules must be involved in the desorption process.

II. EXPERIMENT

The basic features of the apparatus and its operating modes have been described in detail previously.[3] Briefly, the apparatus 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. Condensed molecular layers are grown on the ribbon. All components are housed in an UHV system reaching pressures below 5×10^{-11} Torr. A portion of the negative ions desorbed by electrons impinging on the film are focused by ion lenses at the entrance of the mass spectrometer (MS). Three grids of about 60% transparency are positioned at the entrance of the MS in order 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 are detected as a function of incident 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 derivative of the curve obtained in this latter mode represents the KE distribution of the negative ions studied at the chosen incident electron energy.

In the present experiment, 99.99% pure research grade CO was condensed on the cooled metal substrate and the film thickness was estimated within 50% accuracy by the gas-volume expansion procedure.[8] The energy spread of the electron beam was 0.3 eV and its energy calibrated within

$\pm$ 0.4 eV with respect to the vacuum level, as previously described.[3] 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 data were recorded with incident currents of about 2×10^{-9} A and a target temperature of 20 K.

III. RESULTS

A. O⁻ yield spectra

The dependence of the O⁻ signal on the energy of electrons impinging on a three-layer-thick film of condensed CO is shown on Fig. 1. This curve, which is similar to the one recorded by Sanche,[1] exhibits two peaks with maxima near 12 and ~16 eV, respectively. The latter peak is very broad and seems to contain contributions from more than a single resonant CO⁻ state. In order to understand the differences between this curve and the one observed in DA from gaseous CO, we isolated the CO molecules from the metal substrate by condensing them on a five layer Kr film. Under these conditions, the influence of the substrate on DA reactions, which is due essentially to the effects of the image charge induced in the metal,[9] can be supressed. Thus, it becomes possible with submonolayer CO coverage of the Kr film to obtain only weakly perturbed CO molecules having properties close to those of the free-molecule configuration. Then, by varying the CO coverage from submonolayer to multilayer, the effect of the presence of neighbor CO molecules can be examined. This method is illustrated by the O⁻ ESD yield functions shown in Fig. 2 which were recorded from 0.2(a), 2(b), and 3(c) layers of CO deposited on the five-layer Kr film, respectively. At 0.2 coverage (bottom curve), we obtain, within the energy resolution, a curve which is reminiscent of the one reported in gaseous CO. This result was expected because the influence of the neighboring molecules which is dominant in DA in molecular solids is strongly reduced at submonolayer coverages. At higher CO coverage, the O⁻ yield function changes drastically and seems to contain two distinct contributions: one which is present at low CO coverage and another one at higher electron energy, which must be characteristic of the condensed phase.
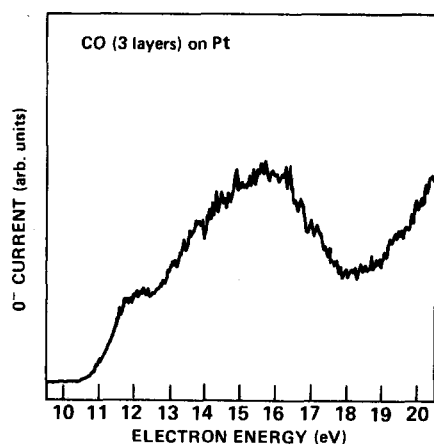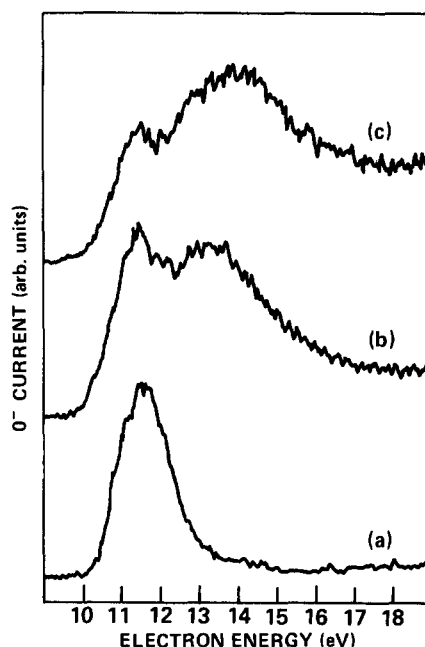

FIG. 2. Energy dependence of the O⁻ yields produced by electron impact on a Pt substrate covered by a five-layer Kr film on which were deposited (a) 0.2, (b) 2, and (c) 3 layers of CO.

B. KE distributions

As shown for O⁻ ESD from condensed O_2[2] and for Cl⁻ ESD from Cl_2,[3] ion-energy spectra appear to be essential to determine the microscopic sequence of step leading to anion emergence in vacuum. We have recorded such spectra (Fig. 3) in the incident electron energy (E_i) range 11–18 eV for a three-layer CO film on Pt. We find that up to 15 eV, the KE
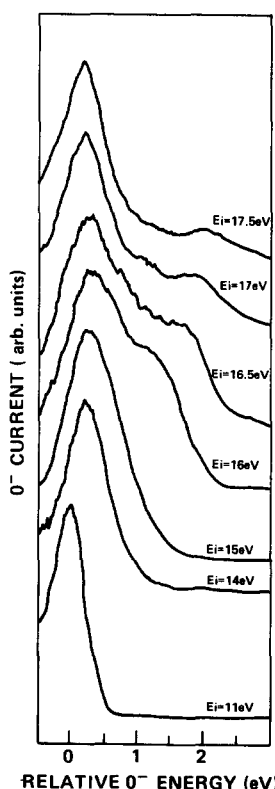

FIG. 3. KE distributions of O⁻ ions produced by electrons of energies $E_i = 11, 14, 15, 16, 16.5, 17,$ and 17.5 eV incident on a three-layer CO film. The ion energy scale is referenced to the maximum in the KE distribution at $E_i = 11$ eV.
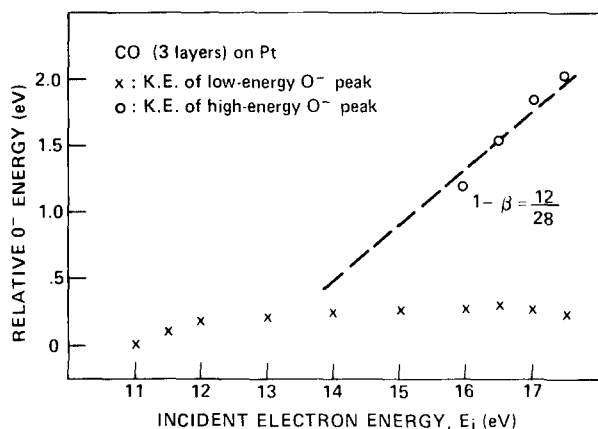

FIG. 1. Energy dependence of the O⁻ yield produced by electron impact on a three- "monolayer"-thick film of CO condensed on a Pt substrate.

FIG. 4. Kinetic energy of the low-energy O⁻ peak (X) and high-energy O⁻ peak (0) in Fig. 3 vs incident electron energy E_i.

distributions exhibit a single maximum with a slightly increasing width toward higher electron energies. Above 15 eV, the ion spectra exhibit two maxima. The one at low energy remains fixed with increasing electron energy and corresponds to O⁻ ions produced with the same KE as those formed below 15 eV. The other shifts toward higher ion energies as the electron energy is increased. The curve representing the KE of O⁻ ions at maxima in the ion spectra as a function of electron energy is shown in Fig. 4. Such a behavior in ion spectra has not been observed previously in ESD.

IV. DISCUSSION

A. O⁻ yield spectra

The results of Fig. 2 strongly suggest that O⁻ production below 13 eV in condensed CO proceeds via the Π CO⁻ resonant states involved in the gas phase. At higher energy, however, the DA signal is characteristic of the condensed phase, and we must therefore search for a mechanism which is absent in the isolated electron–molecule system to explain the appearance of the 13–18 eV signal at higher CO coverages.

We have already observed[1–4] that in the condensed phase, peaks in the anion yield spectra are more numerous than in the gas phase. This has been explained by the existence of $\Sigma^-\leftrightarrow\Sigma^+$ transitions in condensed $O_2 \sim 13$ eV² or by multiple scattering processes involving electronic excitation as in the case of the 11 eV feature[3] in condensed Cl_2. In CO, the lowest electronic excited state a ³Π being located above 6 eV,[10] the latter possibility cannot be involved below electron energies of about 16 eV (i.e., the energy threshold for O⁻ formation by DA plus the energy of the ³Π state). Another possibility could be the existence of a strong resonance associated with a group or cluster of CO molecules [i.e., a $(CO)_n^-$ state], but it is far from obvious how such a state could decay with significant amplitude by O⁻ formation without the additional electron being actually localized on a CO unit. In any case, no such states have even been reported in condensed-phase electron-impact vibrational and electronic excitation studies.[11–13] Consequently, we consider that in condensed CO, DA processes involve Σ^-CO⁻ transient anions. According to Wigner and Witmer correlation

rules two Σ^- resonant CO⁻ states can be formed from the interaction of the ground fragments O⁻ (²P) and C(³P) and one from the fragments O⁻ (²P) and C(¹D). We therefore associate O⁻ production above 13 eV with one or more of these three Σ^- states. We will return to that point after the discussion on the KE distributions.

B. KE distributions

In the case of a DA reaction from a free diatomic molecule the excess reaction energy is shared between the dissociating fragments as KE. The KE of the negative ion fragment is given by

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

where β is the ratio between the mass of the ion and the mass of the molecule, E_i the electron incident energy, Δ the dissociation energy of the neutral molecule, A the electron affinity, and E_n the excitation energy of the neutral fragment. $\beta = 16/28$ for O⁻ ions dissociating from CO.

In order to understand the ion-energy spectra observed for DA in ESD from condensed diatomic molecules, we have to consider the laws of energy and momentum conservation that govern DA processes in a free molecule and the possible changes due to (i) inelastic scattering of the electron before its capture at a molecular site, (ii) the possible existence of transient anions associated with more than a single molecule in the film which would lead to departure from a diatomic-type dissociation, and (iii) the interactions of the dissociated negative ion as it recedes from its site of formation. According to previous arguments on multiple scattering in CO and the possible formation of $(CO)_n^-$ states, we can consider only the PDI of O⁻ ions with the neighboring CO molecules for the interpretation of the ion spectra recorded. It is well known that O⁻ ions interact strongly at low energy with CO molecules to give associative detachment.[14] This process, which can be viewed as inverse DA, proceeds via the ²Π$_u$ CO_2^- resonant state and is represented by the equation

$$O^-(^2P) + CO(^1\Sigma_g) \rightarrow CO_2^-(^2\Pi_u) \rightarrow e^- + CO_2^*. \quad (1)$$
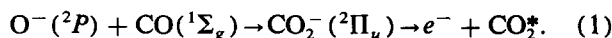
Electron detachment constitutes a particular channel for the decay of the CO_2^- ²Π$_u$ resonant state which can also dissociate to give O⁻ (²P) and CO fragments.[15] Indeed, the recent investigations of isotope exchange in the reaction of ¹⁸O⁻ with C¹⁶O in a flow-drift tube reveals that oxygen exchange competes with detachment.[15] These data indicate that, at thermal energies, 11% of the collisions result in exchange of the oxygen atoms and that as many as 90% of the collisions of O⁻ with CO may be "reactive." Moreover, the cross sections for electron detachment range from 10^{-15} to $\sim 10^{-16}$ cm² for O⁻ scattering from CO at energies near 0 to ~ 5 eV, respectively.[14] This is well within the energy range of the ions produced in the present experiment and we therefore expect O⁻ to react strongly with the surrounding matrix. As mentioned in previous work,[1] reactive collisions are likely to be responsible for the depletion of the O⁻ signal observed in ESD from condensed CO. Furthermore, when dissociation of temporary CO_2^- occurs, the excess energy in

the transient anion must be shared between O^- and CO and this energy partition may involve internal energy of CO. In fact, Chantry[16] who measured O^- ions KE distributions for the DA reaction via the CO_2^- $^2\Pi_u$ resonance has observed that, over the entire anion energy range, the O^- distribution consists of a peak at zero KE with a tail extending toward higher KE. Hence, in condensed CO part of the O^- ions (produced by DA) which interact with surrounding CO molecules are expected to lead to the reaction

$$O^- + CO(^1\Sigma^+) \rightarrow CO_2^- (^2\Pi_u) \rightarrow CO(^1\Sigma^+, v) + O^-. \quad (2)$$
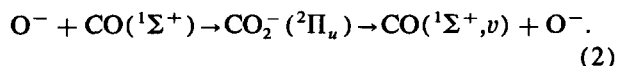
The CO product on the right has acquired vibrational energy in the ground state leaving O^- with less kinetic energy than before the formation of the intermediate CO_2^- state. It follows that the slope of the curve representing the O^- energy vs the incident electron energy for reaction (2) becomes much smaller than 12/28 as observed experimentally (Fig. 4) for the energetic behavior of the low-energy peak of Fig. 3. PDI of O^- via reactive scattering with neighbor molecules forming a condensed film has recently been clearly demonstrated by monitoring OH^- in films containing both O_2 and C_nH_{2n+2} molecules.[17] In these experiments, O^- from DA of O_2 induces the reaction $O^- + C_nH_{2n+2} \rightarrow C_n H_{2n+1} + OH^-$ near the film surface, possibly via an intermediate $(C_nH_{2n+2}O)^-$ state. Following these considerations, we postulate that PDI of O^- ions with CO molecules in condensed CO are responsible for the observed KE distributions up to 15 eV and for the occurrence of the low KE peaks in the ion-energy spectra above 15 eV.

Concerning the high-energy peak in the O^- KE distribution above 15 eV, we notice from Fig. 4 that the plot representing the KE as a function of incident electron energy yields a straight line with slope which compares fairly well with the theoretical value of 12/28 indicating that these ions have practically no interaction with the CO lattice.

In order to confirm the proposed mechanism for O^- ESD from CO molecular solid, we have recorded KE distributions of O^- ions formed with 9 eV electrons impinging on a three-monolayer-thick film containing a mixture of O_2 (5%) and CO (95%) grown on Pt. The curve thus obtained is identical to that recorded for 17 eV electrons impinging on three-layer-thick film of CO. For 9 eV electrons incident on the mixture, O^- formation proceeds via DA reaction at an O_2 site, since O^- production from CO starts only around 10 eV (Fig. 1). These latter O^- ions have about 2.75 eV KE, i.e., the same KE as those formed at 17 eV in pure CO if we assume that the C fragments are in the ^1D excited state. This result indicates clearly that the shape of the anion KE distributions is not due to the initial DA reaction but rather to PDI in the solid. Ions formed with the same amount of KE at an O_2 molecular site in the mixture or at a CO site in pure condensed CO suffer the same interactions as they recede from the CO solid and thereby will have the same KE distributions. This result seems also to indicate that above 15 eV, DA process must be associated with a Σ^- resonant state correlated to $O^-(^2P)$ and $C(^1D)$ fragments at infinite internuclear separation. PDI may also account for the small mag-
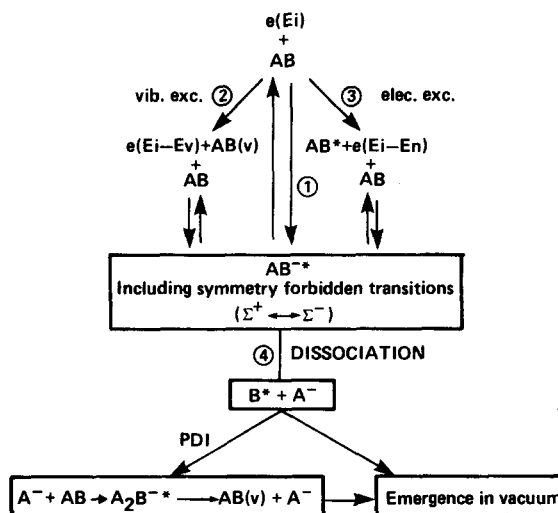

FIG. 5. Possible reaction paths for negative ion electron stimulated desorption from condensed diatomic molecules. Energy losses (E_v and E_n) to vibrational and electronic excitation of electrons (of initial energy E_i) scattered within the solid are shown in paths 2 and 3, respectively. A combination of both paths is also possible.

nitude of the O^- signal recorded in ESD from condensed CO.

V. CONCLUSIONS

This work has contributed to the description of the microscopic sequence of steps that governs O^- emergence in vacuum from DA in ESD from condensed CO molecules. In particular, we have established that PDI of O^- ions with neighboring CO molecules in the solid, which proceeds via an intermediate CO_2^- $^2\Pi_u$ resonant state, modify the KE of O^- ions. As in condensed O_2, we observed DA processes involving transitions which are forbidden in the gas phase by symmetry selection rules. Such transitions appear then to be of common occurrence in the condensed phase and should therefore also be observable in molecular cluster.[18] In recent experiments with $(O_2)_n$ ($n = 1$–15) clusters,[18] the formation of $(O_2)_{n-1}O^-$ ions has been attributed to proceed via the intermediate anion $(O_2)_{n-1} \cdot O_2^-$* (i.e., via the localization of an electron at a molecular O_2 site within the cluster). Thus, in the data of Mark et al.[18] yield spectra of anions resulting from the decay of the intermediate state $(O_2)_{n-1} \cdot O_2^-$ exhibit structure due to the $\Sigma^- \leftrightarrow \Sigma^+$ transition which occur,[2] ~13 eV in condensed O_2.

Considering the present results in CO and those obtained in O_2 and Cl_2, negative-ion ESD from condensed molecules below the energy threshold for polar dissociation involves some or all of the fundamental reactions shown in Fig. 5. Steps 2 or 3 which involve vibrational or electronic multiple scattering will show up in both the KE distributions and the energy dependence of the ion yields whereas PDI modify the KE of the desorbing ions.

ACKNOWLEDGMENTS

[1]L. Sanche, Phys. Rev. Lett. **53**, 1638 (1984).

[2]R. Azria, L. Parenteau, and L. Sanche, Phys. Rev. Lett. **59**, 638 (1987).

[3]R. Azria, L. Parenteau, and L. Sanche, J. Chem. Phys. **87**, 2292 (1987).

[4]L. Sanche and L. Parenteau, J. Vac. Sci. Technol. A **4**, 1240 (1986).

[5]L. Sanche, in *Desorption Induced by Electronic Transitions III*, edited by R. Stulen (Springer, Berlin, 1988).

[6]A. Stamatovic and G. J. Schulz, J. Chem. Phys. **53**, 2663 (1970).

[7]R. I. Hall, I. Cadez, C. Schermann, and M. Tronc, Phys. Rev. A **15**, 599 (1977).

[8]L. Sanche, J. Chem. Phys. **71**, 4860 (1979).

[9]H. Sambe, D. Ramaker, L. Parenteau, and L. Sanche, Phys. Rev. Lett. **59**, 236 (1987).

[10]G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1950).

[11]L. Sanche and M. Michaud, Phys. Rev. B **30**, 6078 (1984).

[12]L. Sanche and M. Michaud, in *Resonances in Electron–Molecule Scatter-* *ing from van der Waals Complexes and Reactive Chemical Dynamics*, edited by Donald G. Truhlar, ACS Symp. Ser. 263 (American Chemical Society, Washington, D.C., 1984), pp. 211–228.

[13]R. M. Marsolais, M. Michaud, and L. Sanche, Phys. Rev. A **35**, 607 (1987).

[14]J. Comer and G. J. Schulz, Phys. Rev. A **10**, 2100 (1974).

[15]J. M. Van Doren, S. E. Barlow, C. H. De Puy, and V. M. Bierbaum, J. Am. Chem. Soc. **109**, 4412 (1987).

[16]P. J. Chantry, J. Chem. Phys. **57**, 3180 (1972).

[17]L. Sanche and L. Parenteau, Phys. Rev. Lett. **59**, 136 (1987).

[18]T. D. Märk, K. Lester, W. Ritter, and A. Stamatovic, Int. J. Mass Spectrom. Ion Phys. **74**, 265 (1986). These authors report the energy dependence of the yields of several oxygen anion formed by electron impact on $(O_2)_n$ clusters. Most of their curves exhibit a broad peak near 13 eV incident electron energy which, according to the result of Ref. 2, can be ascribed to the formation of a Σ^+ symmetry forbidden state.