

Photon-Stimulated Charge Transfer in Condensed O₂ Studied by Negative-Ion Desorption

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Photon-stimulated desorption of negatively charged ions from condensed O₂ is observed in the 17–42-eV photon energy range. Two classes of photon-stimulated charge-transfer processes, i.e., resonant processes via the formation of highly excited states of the condensed molecules and nonresonant processes involving energetic photoelectrons, are considered to account for these observations.

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The charge-transfer process is of fundamental importance to many areas of biology and chemistry. For adsorbed molecules, photon-induced charge transfer may occur either directly by exciting molecular charge-transfer (ion-pair) states or indirectly by attaching a photoemitted electron (issued from the substrate or neighbor adsorbed species) onto the studied molecule. Photon-stimulated charge transfer (PSCT) has been suggested by several authors [1,2] to play an important role in surface photochemistry although no direct evidence of PSCT has been obtained so far.

The aim of this paper is to demonstrate, by using multilayers of condensed O₂ as an example, that negative-ion desorption is a powerful and direct probe of PSCT in adsorbed molecules. The only previously reported observation of negative-ion desorption following photon excitation is that of negative H⁻ ions from a cesiated W(100) surface by Hurych *et al.* [3]. However, in this case the absence of any variation of the desorption signal with photon energy prevented these authors from identifying particular desorption mechanisms. Negative-ion desorption from a number of adsorbed molecules was studied by electron impact [4–6]. Attention was focused on the dissociative attachment of slow electrons on physisorbed or chemisorbed molecules [5].

In this Letter, we report the first study of photon-stimulated desorption of negative ions from condensed gases involving intramolecular charge-transfer (ion-pair) states and intermolecular electron transfer. During the course of this work, Dixon-Warren *et al.* [7] observed for the first time photon-stimulated desorption of negative ions from condensed molecules produced by charge transfer from the substrate.

Synchrotron radiation from Super-ACO at Orsay, dispersed by a grazing-incidence monochromator, is used as a photon source of variable energy in the 17–42-eV energy range with a 0.5-Å bandpass. The experiments are performed in an UHV system reaching pressures below 10⁻¹⁰ mbar. The molecular films are obtained by condensing O₂ on a polycrystalline platinum substrate cooled at 15 K with a liquid-helium flow cryostat. The platinum

substrate is thin enough (20 μm) to be resistively heated in order to be cleaned before any gas deposition. The film thickness of about five monolayers is estimated from photoabsorption measurements. Desorbed positive and negative ions are mass selected through a Riber SQX 156 quadrupole filter and counted as a function of the photon energy. Ion yields are normalized to the photon flux monitored by the photoemission of a gold mesh.

The photodesorption yield of O⁻ from condensed O₂, recorded in the 17–42-eV energy range, is shown in Fig. 1. Resonances superimposed on a slowly increasing continuous background are observed in the low-energy part (17–32 eV), whereas the O⁻ desorption yield rapidly increases beyond 32 eV. Resonances are seen in more detail and are compared with gas-phase data in Fig. 2. We emphasize that some of these resonances (labeled 1–5 in Fig. 2) have a narrow width ranging from 0.4 to 1.4 eV. A broader resonance with a maximum at about 29.8 eV is

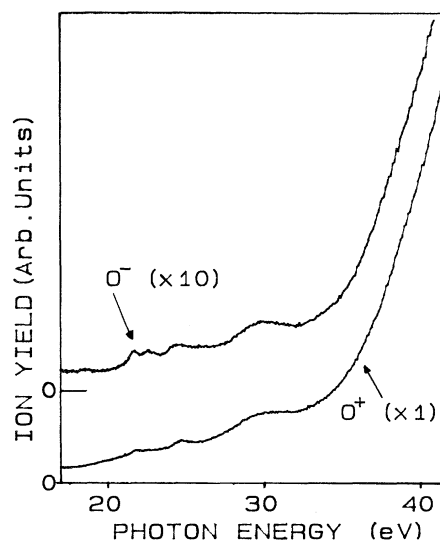


FIG. 1. O⁻ and O⁺ ion yield curves from condensed O₂ (thickness ≈ 5 monolayers).

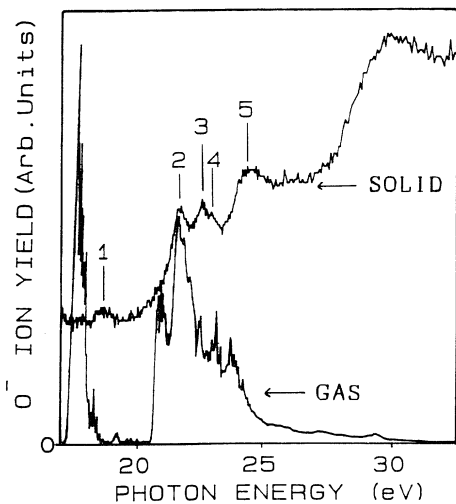


FIG. 2. Comparison of the O^- ion yield curves from condensed O_2 (thickness=5 monolayers) with the O^- ion yield curve from gas-phase O_2 . The gas-phase data are taken from Ref. [8] and are very similar to those of Ref. [9]. Observed narrow resonances are numbered from 1 to 5 and their energies are 18.6, 21.7, 22.6, 22.9, and 24.4 eV, respectively.

also observed.

Similar features, although somewhat modified, are seen in the O^+ ion yield curves of Figs. 1 and 3. At a photon energy of 40 eV the O^+ ion yield is about an order of magnitude larger than the O^- ion yield.

O_2^+ and O_2^- molecular ions are desorbed with a much lower intensity (ion yields relative to that of O^+ are 0.02 and 7×10^{-4} , respectively at a photon energy of 40 eV). The corresponding ion yield curves, shown in Fig. 4, again exhibit a slowly increasing signal between 17 and 32 eV followed by a steep increase beyond 32 eV. We note, however, that the resonances observed in the O^- and O^+ signals between 17 and 27 eV are not discernible in the O_2^+ and O_2^- ion yield curves.

We will now discuss the three main features of the O^- negative-ion desorption: (i) the resonant structures of the ion signal; (ii) the low-energy (17–32 eV) continuum of the ion yield curve; and (iii) the steep increase of the ion yield beyond 32 eV.

The occurrence of resonances in the O^- and O^+ yield curves is a quite surprising result. Resonances, due to the formation of superexcited Rydberg states, are known to exist in the photoabsorption and photoionization spectra of isolated molecules [10]. However, for adsorbed molecules these excited states are expected to be very rapidly quenched before any desorption can occur. The resonances in the O^- and O^+ yield curves of condensed O_2 seem to be blueshifted as compared to the gas phase since the two curves in Fig. 2 show a good band-to-band correspondence if the gas-phase ion yield curve is shifted towards higher energies by about 0.7 eV. Such a blue-

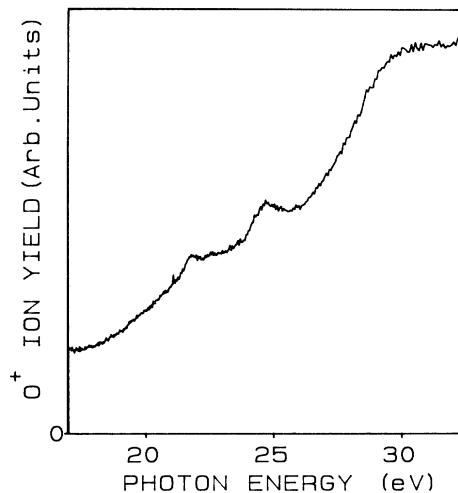


FIG. 3. O^+ ion yield from condensed O_2 (thickness ≈ 5 monolayers).

shift of Rydberg states is also observed in matrices [11] and in rare-gas solids [12]. The gas-phase resonances lying in the 17–19-eV energy range belong to Rydberg series converging to the $b^4\Sigma_g^-$ state of O_2 of which the adiabatic energy is 18.17 eV [8,9,13–15]. The $b^4\Sigma_g^-$ adiabatic ionization energy in solid O_2 is 16.5 eV [16]. The strong gas-to-solid redshift (1.7 eV) of this ionization energy leads to an interesting effect. It appears indeed that the Rydberg resonances in condensed O_2 at about 18.6 eV (peak number 1 in Fig. 2) are lying above the corresponding $b^4\Sigma_g^-$ ionization energy at 16.5 eV. This unusual situation may be explained by a strong cavity

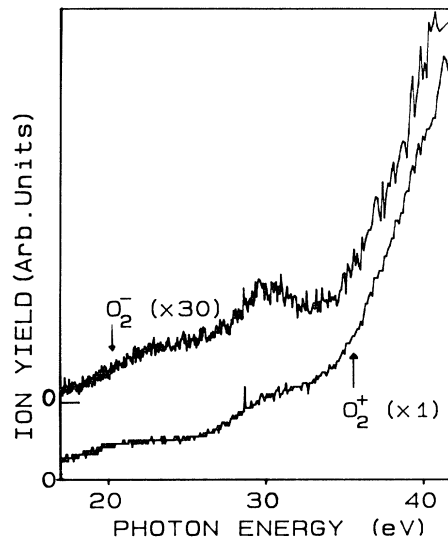
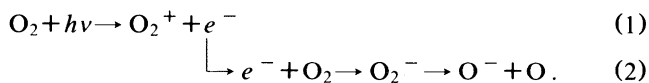


FIG. 4. O_2^- and O_2^+ ion yield curves from condensed O_2 (thickness ≈ 5 monolayers).

effect due to the repulsion between the Rydberg electron and the neighbor O_2 molecules which could maintain the electron in a quasibound state although the internal energy of the system is higher than the ionization energy. This positive-energy Rydberg resonance effect is very similar in nature to the positive-energy states observed above the inner-shell ionization of polyatomic molecules [17]. The gas-phase resonances in the 20–25-eV energy range have been shown [8] to correspond to a shape resonance and to Rydberg and doubly excited Rydberg state series converging to higher ionic states of O_2 of which the energies are unknown in solid O_2 . However, a similar positive-energy-state effect is expected to occur if we assume that the redshift of these ionization energies is comparable to that of the $b^4\Sigma_g^-$ state. It is remarkable that the resonance at 18.6 eV has a much reduced intensity in the O^- ion yield curve from condensed O_2 as compared to that from gas-phase O_2 . However, it is difficult to decide whether this comes from a reduced photoabsorption cross section or from a reduced lifetime of the resonance in the solid. We note that resonances have been observed in the photoionization spectra of O_2 clusters in the same 17–25-eV energy range [18]. However, in this latter case positive ions are mainly issued from direct or indirect single ionization as in gas-phase O_2 , whereas such ionization processes are believed to produce no ion desorption from condensed O_2 [19].

The resonant desorption of O^- and O^+ ions following the formation of Rydberg resonances O_2^* may be ascribed to the ion-pair formation ($O_2^* \rightarrow O^+ + O^-$) occurring either at the surface of the condensed gas or from gas-phase O_2^* molecules expelled from the surface through the action of the repulsive forces from neighbor molecules.

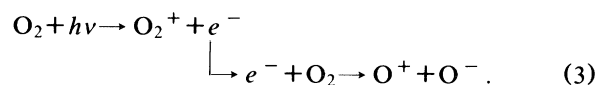
The nonzero O^- signal which underlies the resonances in Fig. 2 may result from several contributions. Some experiments performed with a magnesium filter in front of the sample, allowing suppression of high-order radiation in the 25–50-eV energy range, indicated that the second-order radiation transmitted by the monochromator is only partly responsible for this signal. Ion-pair formation ($O_2 + h\nu \rightarrow O^+ + O^-$), either directly or through the absorption into continuum Rydberg states, for which the threshold energy is expected to be around 16 eV [20] may account for the continuum background signal in the O^- and O^+ ion yield curves of Figs. 2 and 3. However, the steep increase beyond 20 eV in the O^- desorption curve, which seems to be absent in the O^+ one, is believed to be due to the following photoelectron-induced process:



According to these reactions a photoelectron emitted from an O_2 molecule may interact with another molecule via dissociative attachment. It is known indeed from photoemission spectroscopy of solid oxygen [16] that the

kinetic-energy distribution of photoelectrons issued from reaction (1) is dominated by the ionization from the $1\Pi_u$ orbital of O_2 . This gives an effective threshold energy of the kinetic-energy distribution at about $h\nu - 15$ eV although there exists an ionization potential energy of solid O_2 lower than 15 eV. The electron dissociative attachment (reaction 2) has an onset energy of about 5 eV. It follows that the desorption of O^- according to reactions (1) and (2) is expected to have a threshold energy around 20 eV, which fits well with the observed threshold energy in Fig. 2 at about 20 eV. As long as the two O_2 molecules involved in reactions (1) and (2) are far enough from each other to be free of any interaction, the photon energy dependence of reactions (1) and (2) is believed to be a convolution of the kinetic-energy distribution of the photoelectrons from reaction (1) with the electron energy dependence of reaction (2). This is expected to give rise to very broad features having a width of at least 3–5 eV. This definitively precludes the assignment of the narrow resonances in Fig. 2 to such processes.

The strong increase of the O^- and O^+ desorption yields above 32 eV may be ascribed to the following reactions:



Reaction (3) (direct ion-pair formation) is known to have an onset energy around 16 eV [20]. This agrees well with the threshold energy for reactions (1) and (3) of around 31–32 eV.

We note that the singly charged O_2^+ ions produced in reaction (1) are believed to be rapidly neutralized by resonant charge exchange and to produce no ion desorption [19].

The O_2^- and O_2^+ ion yield curves of Fig. 4 look very similar to the O^- and O^+ curves with the exception of the narrow resonances. We note in particular the steep increase beyond 32 eV. This suggests that desorbed O_2^- and O_2^+ ions are issued from the same primary processes as the O^- and O^+ ions, respectively. From electron-stimulated-desorption studies of condensed O_2 [21] it was concluded that the O_2^- desorption mainly results from the post-dissociation interaction (PDI) of a produced O^- ion with a neighbor O_2 molecule. This may also be valid here since the relative intensity of O_2^- ions as compared to O^- ions is very similar to that observed in the electron-impact experiment [21]. Similarly, the O_2^+ desorption may result from the PDI of O^+ ions with neighbor O_2 molecules.

We emphasize that the resonances lying in the 17–27-eV energy range of the O^- and O^+ ion yield curves (Figs. 2 and 3) seem to be absent from the O_2^+ and O_2^- ion yield curves (Fig. 4). This indicates that PDI processes would not be efficient for O^+ and O^- ions issued from the relaxation of these resonances. It is known from gas-phase experiments [21] that the PDI process has a

threshold energy near 1-eV center-of-mass energy. It may thus happen that, for those resonances which are not visible in Fig. 4, the kinetic energy of the O^- ions is not sufficient to induce the PDI reaction (and similarly for the O^+ ions).

In conclusion, these results suggest the existence of two classes of charge-transfer processes: (i) resonant processes occurring through the formation of highly excited states of the condensed molecules, and (ii) nonresonant processes induced by energetic photoelectrons. Much further work, including the kinetic-energy analysis of desorbed ions and experiments performed with mixed condensed gases, will be necessary in order to explain in detail these new processes. The resonant processes are of particular interest since they give evidence of highly excited states which could not be observed by other methods. Such resonant states lying between 6 and 12 eV above the lowest ionization energy of condensed O_2 [16] are believed to be derived from O_2 superexcited Rydberg states which are known in isolated gas-phase molecules, however, with different lifetimes and energies. The photoelectron-induced processes also reveal important features of the photon-stimulated reactions in condensed molecules. Negative-ion photodesorption is a new and powerful way for probing the role of photoelectrons in surface photochemistry.

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