Electron-Induced Synthesis of Ozone in a Dioxygen Matrix

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Ozone (O_3) was synthesized in the condensed phase induced by electron bombardment of multilayer films of molecular oxygen condensed at temperatures below 30 K on metal surfaces. O_3 formation was demonstrated by the observation of the asymmetric stretching (ν_3) and bending (ν_2) normal modes of vibration in a high-resolution electron energy-loss spectroscopy experiment, and by characteristic changes in electron-stimulated desorption of O^-. The threshold electron energy for the O_3 formation is found at 3.5 ± 0.2 eV. It corresponds to the formation of $O(^3P)$ associated with $O^-(^2P)$ by dissociative electron attachment at condensed O_2, followed by the third body reaction $O + O_2 + O_2 \rightarrow O_3 + O_2$. Above 5.1 eV bombarding energy, dissociative excitation of the O_2^* ($c^1\Sigma_u^-, C^3\Delta_u, A^3\Sigma_u^+, B^3\Sigma_u^-$) states is the main source of atomic oxygen $O(^3P)$ or $O(^1D)$ involved in the O_3 synthesis. [S0031-9007(97)03622-3]

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Multilayers of molecules condensed at temperatures below 30 K on bulk surfaces are of great interest since they simulate a situation in the interstellar clouds. These clouds consist of matter in gaseous form and, to a much smaller amount, in the form of tiny dust particles well capable of carrying layers of physisorbed gases at the low temperature in the clouds [1]. It is well accepted that interstellar molecules are synthesized via gas phase reactions and via reactions occurring at the surfaces of the dust particles [1]. We report here on the synthesis of ozone (O_3) in a multilayer of dioxygen (O_2) condensed at a metal surface at $T < 30$ K under ultrahigh vacuum (UHV) in the laboratory.

The interaction of low-energy electrons with a molecular adsorbate produces highly reactive species (radicals, cations, and anions) via reactions such as dissociative electron attachment (DEA), ion-pair formation or molecular (pre)dissociation [2]. These species can react with neighboring molecules to form new products. So far, only ion-molecule reactions mediated by electron impact have been observed in condensed phases [2]. In this Letter we present a case of electron-induced adsorbate modification via atom-molecule reaction for the first time. In particular, we report on ozone synthesis induced by electron bombardment in a layer of condensed dioxygen. This reaction was probed by two different techniques: high resolution electron energy loss spectroscopy (HREELS) performed in Berlin and electron-stimulated desorption (ESD) performed in Orsay.

The experiments were performed under UHV conditions in the following way: A multilayer of O_2 was condensed onto an Ag(111) single crystal (for HREELS) or a poly-crystalline Pt sample (for ESD) cooled to $T < 30$ K by continuous He flow. The film was then bombarded with an electron beam of energy E_b for some time and then analyzed by HREELS and O^- ESD. The two apparatus have been described in detail elsewhere [3,4]. The pressure in the HREEL spectrometer (Delta 0.5 Vacuum Science Instruments, Germany) was in the 10^{-11} mbar range during electron bombardment and recording the spectra. Under these conditions the O_2 film remained clean during all procedures. The HREEL spectrum, measured even after several hours, did not display any structures other than those characteristic of O_2. The monochromator was used successively to bombard the sample and then to perform HREEL measurements. In order to bombard the sample with sufficiently high electron current, the energy resolution was set to 13 meV. It could be set to 2.5 meV, but in most cases it was left at 13 meV in order to save time. During the ESD experiments the pressure in the chamber was about 2×10^{-10} mbar. The desorbing anions were mass analyzed and detected by means of a quadrupole mass spectrometer. The energy of the incident electrons is given with respect to the vacuum level and was calibrated within ± 0.2 eV as described in Ref. [4].

Figure 1 shows two HREEL spectra of an O_2 film after electron bombardment whose characteristics are given in the figure captions. The HREEL spectra themselves were measured at an incident energy $E_0 = 7$ eV [Fig. 1(a)] and 3 eV [Fig. 1(b)] in specular geometry. In the range from 0 to 260 meV, the spectra display the peak of the elastically scattered electrons and three energy losses at 192.8 ± 0.2 meV, 128.6 ± 0.5 meV, and 86 ± 2 meV. Measurements (not shown) performed at $E_0 = 7$ eV in

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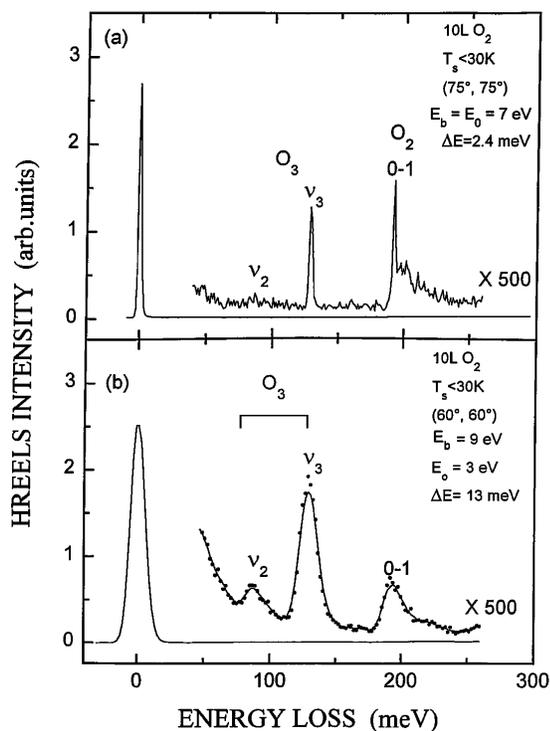
FIG. 1. HREEL spectra of O_2 films prepared by dosing 10 L O_2 (1 L = 10^{-6} mbar sec) onto an Ag(111) surface at a temperature $T_s < 30$ K. (a) The film was bombarded with an electron beam of a current of about 30 pA and an energy of $E_b = 7$ eV during 8 h. The spectrum was recorded with a primary energy $E_0 = 7$ eV in specular geometry (75° in and 75° out with respect to the surface normal). The full width at half-maximum of the energy of the elastically scattered electrons was set to 2.4 meV. (b) The film was bombarded with an electron beam of a current of about 1 nA and an energy of $E_b = 9$ eV during 45 min. The spectrum was recorded with a primary energy $E_0 = 3$ eV in specular geometry (60° in and 60° out with respect to the surface normal). The full width at half maximum of the energy of the elastically scattered electrons was set to 13 meV.

nonspecular geometry did not display any structure besides the 192.8 meV peak. This shows that the two losses at 128.6 and 86 meV are dipole active [5]. The structure centered at 192.8 meV (Fig. 1) is due to the excitation of the intramolecular stretching mode of physisorbed O_2 which is excited via a shape resonance so that the detection of the according energy loss is not confined to the specular beam. Its strong asymmetry is attributed to the excitation of coupled low-frequency modes (translation, rotation) as described elsewhere [3]. By comparison with Fourier transform IR spectroscopic data [6], the other two peaks can be identified as the two characteristic modes of O_3, the asymmetric stretching mode (ν_3), and the bending mode (ν_2), respectively. This assignment is confirmed by very recent EELS measurements of the vibrational modes of O_3 in the gas phase [7]. The relative intensities of the O_3 modes are enhanced at the smaller probing energy in Fig. 1(b). This may be due to the presence of the O_3^{*-} resonance at about $E_0 = 3$ eV [7].

The simplest mechanism for O_3 synthesis, induced by low-energy electron impact onto an O_2 multilayer, consists of the following two reaction steps:

$$O_2(X^3\Sigma_g^-) + e^- \rightarrow O(^3P) + O^-(^2P) \text{ or } O(^3P) \text{ or } O(^1D)$$
$$(1)$$
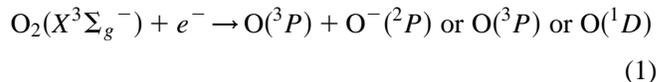
which proceeds either via a DEA reaction [8] or via dissociative excitation involving the O_2^* $c^1\Sigma_u^-, C^3\Delta_u, A^3\Sigma_u^+$ states (Herzberg states) [9] or the $B^3\Sigma_u^-$ bands and the Schumann-Runge continuum of O_2 [10]. The first step is then followed by

$$O(^3P) + O_2(X^3\Sigma_g^-) \rightarrow O_3(^1A_1).$$
$$(2)$$
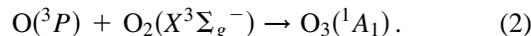
The second reaction is exothermic and requires the presence of a third body [11], provided here by the surrounding O_2 molecules.

The electron-induced synthesis of O_3 was further checked by ESD, i.e., by a completely independent experimental method. Figure 2 shows the O^- yield as a function of energy of the incoming electrons before [Fig. 2(a)] and after [Fig. 2(b)] bombardment with an electron beam of 10 eV energy and 10 nA current during 30 min. Above 5 eV, the two curves are similar. The O^- signal is characteristic of O^- ESD from condensed O_2 via DEA processes involving the $^2\Pi_u$ and $^2\Sigma_g^+$ O_2^{*-} resonance states [8,12]. We see from Fig. 2(b) that, after bombardment, an O^- signal appears in the 2–5 eV range. As in this energy range, an O^- ESD signal from a pure O_2 film is not observed; we assign this signal to a decomposition product of the ozonide O_3^- anion. It is known from experiments in O_3 gas [7,13] that O^- formation proceeds via DEA reactions and presents maxima at 0.4, 1.3, 3.2, and 7.5 eV incident energy which correspond to O_3^{*-} resonance states. At 0.4 and 1.3 eV, O^- anions are formed with very low kinetic energy (<0.5 eV). Such low-energy ions cannot be observed in an ESD
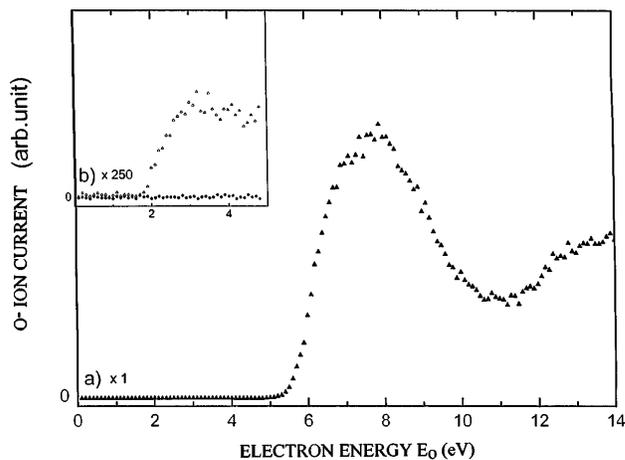
FIG. 2. O^- anion yield as a function of the incident electron energy E_0 from condensed O_2; (a) full spectrum before bombardment; (b) comparison in the 0–4.8 eV energy range between curve (a) (•) and the spectrum after irradiation of the film at $E_b = 10$ eV (△).

experiment due to the polarization barrier induced in the condensed phase [2,14]. Near 3.2 and 7.5 eV, O^- anions are formed with higher kinetic energy (>1.5 eV) so that they are able to desorb. The 7.5 eV DEA process in O_3 is superimposed with DEA processes in O_2 and, therefore, cannot be a signature of O_3 in a O_2-O_3 mixture. However, this is not the case for the 3.2 eV process. Therefore we attribute the O^- signal, observed at low energy in Fig. 2(b), to O_3 produced by electron bombardment of the O_2 adsorbate.

This assignment is further supported if we consider the process of O_2^- ion formation in gaseous O_3. In gaseous ozone O_2^- anions are formed with a kinetic energy of about 2 eV [13]. We have observed that, after electron bombardment of an O_2 adsorbate, the O_2^- ESD signal about 7.5 eV [15] increases by a factor of 2 to 3 as the result of O_3 synthesis. These results will be published later.

In Fig. 3 we report the efficiency of the O_3 synthesis as a function of the energy of the bombarding electrons. In HREELS experiments this efficiency is defined as the intensity of the ν_3 peak relative to that of the elastically scattered electrons. In ESD experiments it is expressed as the intensity of the O^- signal measured at a probing energy $E_0 = 3.5$ eV. The energy threshold for the O_3 production measured in ESD is 3.5 ± 0.2 eV, in agreement with the HREELS result. According to reactions (1) and (2), the onset energy for O_3 synthesis must be associated with the onset for the production of the $O(^3P)$ atoms. The O_2 dissociation energy is equal to 5.1 eV, therefore dissociative excitation of O_2 cannot account for the observed onset at 3.5 eV. This value corresponds very closely to the measured threshold for surface charging of condensed O_2 via the $^2\Pi_u O_2^-$ resonance state, leading to the formation of $O(^3P)$ atoms and O^- (^2P) anions, which remain trapped at the surface of the O_2 film [2].
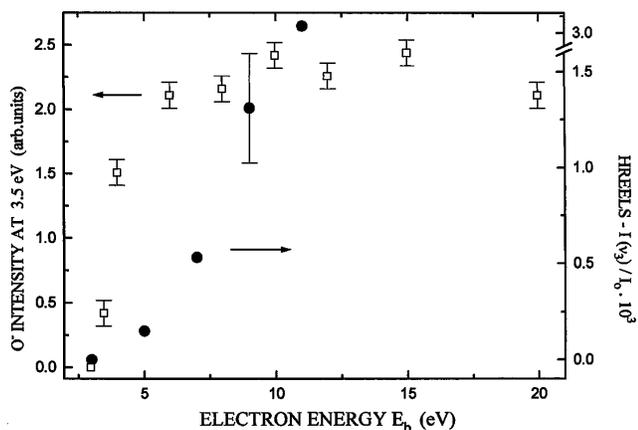
FIG. 3. Efficiency of the O_3 synthesis as a function of the bombardment energy E_b obtained by ESD (open squares, left axis) and HREELS (filled dots, right axis) measurements. The conditions of bombardment and recording are the same as in Fig. 1(b) (except E_b, which varies).

Above the onset at 3.5 eV, the efficiency for O_3 synthesis increases as the other two mechanisms, the excitation of the Herzberg states and of the Schumann-Runge state, become operative. Indeed, as in the gas phase, we may expect that the cross section used to create $O(^3P)$ or $O(^1D)$ atoms is higher via the excitation of the Herzberg and Schumann-Runge states than via the DEA.

Above the threshold (see Fig. 3), the efficiency increases and reaches a kind of plateau around 10 eV in ESD of O^-, while it rises steeply in HREELS. These differences are attributed to the intrinsic differences of the two techniques used to probe O_3 since the technique used to produce ozone (electron bombardment) is the same in both experiments. In HREELS both the surface and the bulk of the film are analyzed [5], whereas in ESD only the topmost layer contributes significantly to the desorbed signal [16]. Since the number of O_2 molecules available for the ozone production is very large in the bulk and limited in the topmost layer, we may expect that the first layer of the film is faster saturated in O_3. Moreover, the number of O_3 species is stable in the topmost layer if the fragments of O_2 dissociation do not leave the surface, e.g., for bombardment energies E_b below 5 eV. O_3 molecules may themselves be decomposed by continuous electron bombardment. Decomposition of O_3 in the topmost layer leads to the desorption of fragments, while decomposition in the bulk may give rise to the production of new O_3 by the collision of fragments with O_2 neighbors. Thus, an equilibrium between electron-induced synthesis and decomposition of O_3 leads to a rapid saturation of the number of O_3 molecules produced in the topmost layer as seen in the ESD experiment. However, in the bulk, the number of synthesized O_3—neither limited by the number of O_2 molecules nor by O_3 decomposition—increases continuously in the studied energy range, as seen in the HREELS experiment.

In conclusion, the electron bombardment of a molecular film induces strong chemical modifications of the media. We have shown, in particular, that ozone is efficiently synthesized in condensed O_2 by low-energy electron bombardment. This reaction may well play a role in the dust particles in the interstellar clouds, where the vacuum ultraviolet field may create the appropriate electrons. More generally, in all studies concerned with electron impact on condensed molecules, such chemical reactions may take place and influence the experimental results.

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