Surface Enhanced Photodissociation of Physisorbed Molecules

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We have investigated the photon stimulated desorption of ions from physisorbed layers of CO and O_2 on graphite using VUV synchrotron radiation in the range of 13 to 35 eV. In both systems we find a significant enhancement in the monolayer regime of the desorption of O^- ions via resonant states which correspond to direct molecular photoabsorption. This enhancement, which is accompanied by suppression of positive ion desorption, is attributed to surface electron attachment following molecular photoexcitation.

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One of the principal results emerging from the new experimental studies of surface photodynamics is the possibility of "substrate-mediated" photodissociation or photodesorption—electrons (or holes) photoexcited in the substrate drive the desorption process [1–4]. The experimental interest in these new desorption channels is mirrored by the emergence of a distinct theoretical effort to describe desorption via electron transfer [5,6]. One important mechanism is the dissociative attachment of photoemitted electrons to adsorbed molecules [7]; work with low energy electron beams shows that tuning the electron energy to a specific molecular negative ion resonance state results in efficient bond rupture [8,9] or vibrational excitation [10,11]. However, from the viewpoint of applications, e.g., chemically selective surface modification, direct molecular dissociation, or desorption is more promising than a substrate-mediated process; in the case of direct excitation, the wavelength dependence of the process is resonant (and hence chemically specific) because it reflects a specific intramolecular photoexcitation event, as in the free molecule. In this Letter we report a study of photon stimulated desorption from physisorbed layers of CO and O_2 on graphite, using VUV synchrotron radiation in the range 13 to 35 eV, which finds that resonant photodissociation of both molecules is enhanced in the monolayer regime. This enhancement, evident in the negative ion yields (O^-), is associated with a suppression of the corresponding positive ion desorption, and leads us to propose a new mechanism based on surface electron attachment following direct molecular photoexcitation.

The experimental results were obtained at beam line 3.1 of the Daresbury Synchrotron Radiation Source. Synchrotron light was dispersed in the energy range 13–35 eV with a 1 m Seya-Namioka monochromator incorporating a 2400 lines mm^{-1} ruled grating. The bandpass of the monochromator optics was set at 6 Å in order to enhance the photon flux. Below 20 eV this corresponds to an energy resolution of better than 0.2 eV. From 20 to 35 eV the resolution is still below 0.6 eV.

Desorbed positive and negative ions were detected by a pulse counting quadrupole mass spectrometer, described previously [12]. The background signal, given by the signal at mass 15, was subtracted from the data. The highly oriented pyrolytic graphite (HOPG) substrates were mounted on a liquid helium cryostat in an ultrahigh vacuum chamber and cleaned by electron bombardment heating. The calibrated base temperature of the sample, measured with a four-wire rhodium-iron resistance thermometer, was 29 K. Gas dosing was accomplished by filling the chamber with $\sim 2 \times 10^{-8}$ mbar of CO or O_2. All experiments were conducted at a residual gas pressure below 5×10^{-10} mbar. The ion yields were measured as a function of both photon energy and coverage (i.e., exposure).

Figure 1 shows the yield of O^- ions photodesorbed from a submonolayer coverage of CO physisorbed on graphite at 29 K. A well-defined resonance is observed, centered at 22 eV. This resonance feature has been

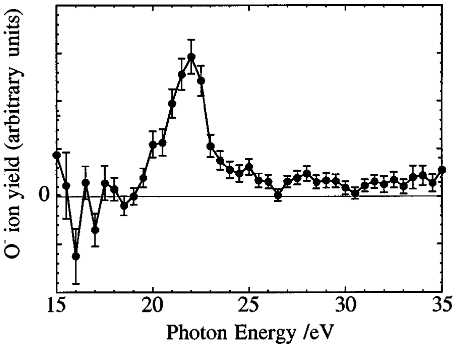

FIG. 1. Photon stimulated desorption yield of O^- ions from submonolayer (3 L) CO physisorbed on graphite as a function of photon energy.

observed both in gas phase studies [13] and in the photodesorption of O^- from physisorbed CO/Pt(111) [14]. Thus the resonance clearly arises from the direct photoexcitation of the physisorbed CO molecule. The sharp resonance feature is not compatible with absorption of light in the substrate. The yield of C^+ ions also shows a resonance at 22 eV, both on graphite and Pt(111) [14] and in the gas phase [13]. The mechanism of photodissociation is thus direct dipolar dissociation, which yields the ion pair C^+/O^-,

$$\mathrm{CO} + h\nu \rightarrow \mathrm{CO}^* \rightarrow \mathrm{C}^+ + \mathrm{O}^- .$$

The gas phase measurements reveal seven intense photoabsorption bands in the photon energy range 20.9 to 22.5 eV, assigned to the predissociation of $3ds$ and $3ps$ Rydberg states converging to the $D^2\Pi(5\sigma)^{-1}(1\pi)^1(6\sigma)^1$ state [13].

Of particular interest in the present study is the coverage dependence of the ion yields. Figure 2 shows the O^- and C^+ signals as a function of CO exposure at 29 K, where a multilayer can be grown on the surface. Measurement of the same ion yields at 42 K, above the multilayer desorption temperature (i.e., where only one monolayer can be grown), allows us to assign the completion of the monolayer in Fig. 2 to an exposure of approximately 6 L ($1\ \mathrm{L} = 10^{-6}$ Torr s) [15]. The negative ion (O^-) yield in Fig. 2 increases as a function of exposure in the submonolayer regime [15] but clearly falls away in the multilayer. Thus the yield of O^- ions is enhanced in the submonolayer regime. By contrast, the yield of C^+ ions is zero until a coverage of 4 L is reached; at this point the signal rises and remains high in the multilayer regime. Note that the threshold for C^+ desorption at 4 L matches the peak in the yield of O^- ions. *It is therefore logical to associate the enhanced yield of* O^- *ions in the submonolayer regime with the suppression of the* C^+ *yield.*

In searching for a mechanism which could account for the striking behavior observed, it is valuable to consider recent gas phase studies of electronically excited target molecules [16–21], which suggest the possibility of surface electron attachment to the photoexcited physisorbed molecule. The gas phase experiments have shown significant enhancements in the electron attachment cross sections, from a factor of 3 or 4 for low lying electronically excited states [16] to 7 or 8 orders of magnitude for superexcited states (where the energy of the excited state exceeds the first ionization energy of the molecule) produced by multiphoton laser excitation [17]. These observations suggest that electron attachment from the substrate to the excited adsorbate may be a very efficient process. The gas phase data also indicate that the cross section is highest for electrons of very low (<0.5 eV) kinetic energy [18]. In this light, resonant tunneling of electrons from below the Fermi level of the substrate into the photoexcited physisorbed CO molecule is an appealing possibility. Electron attachment would suppress the C^+ signal (by neutralization) and could enhance the O^- signal—since some of the energy released by neutralization could be channeled into kinetic energy of the O^- ion [7]. The electron tunneling would also restrict the mechanism to the first monolayer, as observed. Of course, in speaking of substrate electron attachment to a photoexcited adsorbed molecule we do not mean to insist on a strictly two step process, i.e., (i) molecular photoexcitation followed by (ii) electron attachment. It is possible that these two events may occur simultaneously, a process which might then be described, in other language, as direct resonant photoexcitation of a charge transfer state of the molecule-surface system.

The generality of the kind of behavior evident in the CO/graphite system is confirmed by Fig. 3, which shows the yield of positive ions (O^+) and negative ions (O^-) from 5 L of O_2 on graphite as a function of photon energy. Like the O^- signal from CO, Fig. 1, the O^- signal from O_2/graphite shows a well-defined resonance, centered at 15.3 eV and with a FWHM of 1.2 eV. There

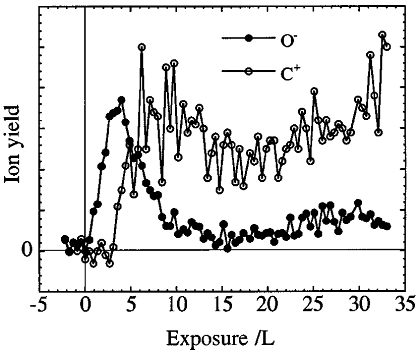

FIG. 2. The yield of O^- and C^+ ions photodesorbed from CO/graphite as a function of exposure for a photon energy of 22 eV.

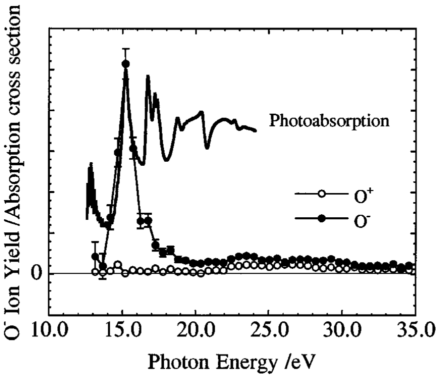

FIG. 3. Photon stimulated desorption yield of O^- ions from 5 L of O_2 physisorbed on graphite as a function of photon energy. Also shown is the gas phase photoabsorption cross section (with resolution broadened, see text) normalized at 15.3 eV (from [23]).

is no detectable O^+ signal below 20 eV, although the weak structure above 20 eV in the negative ion spectrum is also observed in the O^+ yield. The resonance at ~15 eV has not been observed in previous studies of photon stimulated desorption from O_2/graphite. Reference [22] reported photodesorption from low coverages of O_2/graphite, but was restricted to ions of high kinetic energy [12]. Reference [12] reported photodesorption from higher coverages of O_2/graphite than those employed here, where the wavelength dependence of the ion yield is quite different. Figure 4 shows that the yield of O^- ions at a photon energy of 15 eV falls off sharply at higher coverages, just as in the case of CO.

In the case of O_2/graphite, unlike the CO/graphite system, the resonance in the O^- yield does not correspond to a resonance in the gas phase photodissociation yield. Indeed, the resonant feature at 15.3 eV falls *below the thermodynamic threshold* for gas phase production of O^-, which occurs at 17.3 eV [14]. However, the resonance observed in the O^- yield of Fig. 3 does correspond to a feature in the measured gas phase photoabsorption cross section [23], also shown in Fig 3 with the resolution broadened to match that of the photodesorption experiment [24]. The correspondence is consistent with an initial photoexcitation of the physisorbed O_2 molecule similar to that in the free molecule, where the resonance is assigned to a series of Rydberg states converging to the $O_2{}^+$ $a^4\Pi_u$ threshold [23]. Since the photoexcited state is neutral, and the molecule is physisorbed, the expected shift in the energy of the resonance from the gas phase to the surface is at most 1 eV, on the basis of matrix experiments [25]. For comparison, the energy shifts of *charged* O_2 states on the surface are themselves only 1.5 eV [26].

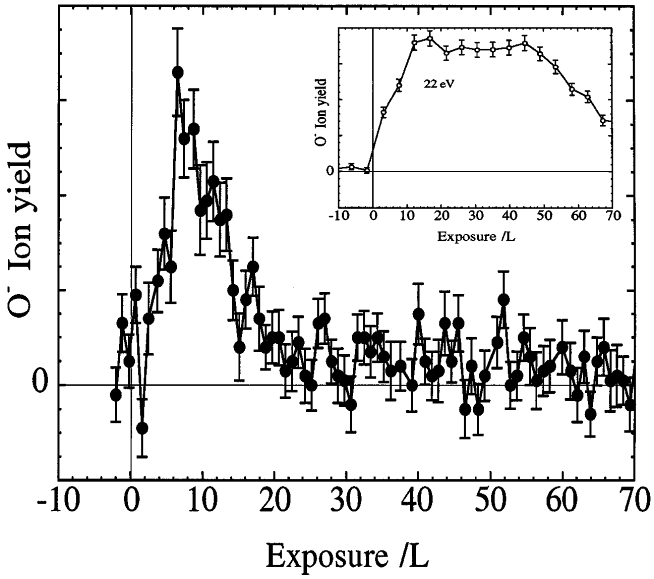

FIG. 4. The photodesorbed O^- ion yield from O_2/graphite as a function of exposure for a photon energy of 15 eV and (inset) 22 eV.

The experimental results from physisorbed O_2 provide a stringent test of the suggested mechanism for the enhanced O^- yield from CO/graphite in the monolayer regime, i.e., surface electron attachment following photoexcitation of the physisorbed molecule. In both cases a resonance is observed in the negative ion yield corresponding to a photoabsorption resonance in the free molecule and the negative ion signal is enhanced in the monolayer regime, and in both cases the positive ion signal is absent, but the mechanism must also account for the appearance of O^- ions below the gas phase thermodynamic threshold energy. The proposed mechanism is consistent with the lower threshold for dissociation, because the energy released by neutralization of the O^+ fragment will lower the dissociation limit [27]. If the disocciation limit is dragged down in energy below the photoabsorption resonance at 15 eV, then photodissociation via this channel is "switched on."

The photodesorption results for O_2/graphite are also consistent with electron stimulated desorption (ESD) studies of the same system [28]. In particular, the threshold for production of O^- ions in the saturated monolayer phase is pulled down from the gas phase value 17.3 eV to 15 eV, exactly as predicted by the present results. Moreover, Sanche [8] reported ESD results indicating an enhancement of the cross section for dipolar dissociation of O_2 condensed on polycrystalline Pt at lower coverages, and speculated that this behavior might be associated with neutralization of the O^+ fragment, although the experimental apparatus did not allow the detection of positive ions.

In summary, we have observed a resonance in the yield of O^- ions photodesorbed from both CO and O_2 physisorbed on graphite. In the case of CO, the resonance is assigned to direct dipolar dissociation of the molecule, as in the gas phase. The yield of negative ions (O^-) is significantly enhanced in the submonolayer regime, and this enhancement is associated with a suppression of the positive ion (C^+) yield. The results are consistent with surface electron transfer following molecular photoexcitation, as suggested by gas phase experiments which show hugely enhanced cross sections for electron attachment to electronically excited molecules. Similar behavior is observed in the O_2/graphite system except that in this case the resonance observed lies below the gas phase thermodynamic threshold for production of O^-. A lowering of the dissociation limit is consistent with electron transfer. Future experiments will need to address the issue of *state selectivity,* e.g., why the O_2 gas phase photoabsorption resonance at ~15 eV couples to O^- desorption from the surface while other resonances (e.g., at ~17 eV) do not—which may relate to the detailed symmetry of the electronically excited molecular states [29]—and to explore the influence of the image potential on the desorbing ions [30]. Finally, the model proposed here is not restricted to physisorbed molecules, and it will be intriguing to explore the possible extension of the effects reported to chemisorption systems.

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