Photoinduced Ejection of Ballistic Oxygen Atoms from N_2O Adsorbed on Pt(111)

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Polarized ultraviolet light from an excimer laser (193 nm) was used to photodissociate N_2O adsorbed on an 80 K Pt(111) surface. The release of ballistic oxygen atoms, a prompt axial recoil with no collisions with neighboring adsorbates, was seen along the tilted N_2O molecular bond axis. The ballistic oxygen atoms leave the surface either in the ground state (^3P) or in the first electronically excited state (^1D). The kinetic energy of the $O(^3P)$ and of the $O(^1D)$ photoproducts is similar (0.5 eV), suggesting a common dissociative intermediate.

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One of the most spectacular aspects of photon or electron induced chemistry of adsorbates on solid surfaces is the ejection of fragments along specific directions determined by the spatial orientation of the bonds broken at the surface. A well-known example is the angular distribution of the electron-stimulated desorption ion angular distribution of H^+ (ESDIAD) from ammonia-covered surfaces, which provides unambiguous information about the azimuthal position of NH_3 with respect to the surface registry [1]. In general, much less energy is available in photon-stimulated desorption, and it is not clear whether such drastic events may still occur. We have focused our attention on the photochemistry of N_2O/Pt(111) for the following reasons. First, the gas phase photolysis of N_2O into N_2 and O fragments is well known [2–7]. Second, low energy (1–4 eV) electron attachment to molecular N_2O is known to yield N_2 and O^- fragments, a process driven by the strong electron affinity of oxygen [8]. Electrons created at a metal surface by the absorption of uv light have energies in the same range. Third, a rich variety of photochemical processes have been found for N_2O/Pt(111) [9–11]. These well-documented data provide a sound basis to compare and contrast the mechanisms observed in the gas phase to those observed for the same molecule condensed on a solid surface.

Vibrational (electron energy loss) spectroscopy studies of N_2O/Pt(111) suggest that N_2O is tilted at 35° from the surface plane with the O atom pointing outward [12]. The release of ballistic oxygen atoms, i.e., a prompt axial recoil with no collisions with neighboring adsorbates, from this bonding geometry should show a significant lobe along the tilted N_2O molecular axis. Here, we report the first clear evidence of photoinduced axial recoil of atomic fragments from an adsorbed molecule. Ballistic oxygen atoms are ejected in both the ground $O(^3P)$ and first excited $O(^1D)$ states. We believe that this is also the first observation of electronically excited species being photodesorbed from a metal surface, a surprising result in view of the ability of a metal surface to rapidly quench electronic excitations. Our results suggest that both $O(^3P)$ and $O(^1D)$ are produced from a common dissociative intermediate.

The experiments were done with the Pt(111) surface clamped on a liquid nitrogen cooled cryostat and under UHV conditions. The temperature of the crystal was measured to be 80 K after cooling, well below the observed desorption temperature of N_2O, 97 K, but above the multilayer condensation temperature, 70 K [9]. The Pt(111) crystal was dosed with N_2O from a pulsed molecular beam producing a spot size of about 2–3 mm in diameter at the surface. The adsorbed N_2O was illuminated by p-polarized uv light (<1 mJ/cm^2) from an excimer laser (193 nm, $h\nu = 6.4$ eV) at a glancing incidence angle of 15° from the surface plane. The photoproducts were detected with resonantly enhanced multiphoton ionization spectroscopy at a distance of 1.4 cm from the surface (the distance was found by moving the crystal with the manipulator until it blocked the probe laser beam). For oxygen atoms, the excited $O(^1D)$ state was ionized by a resonant (2 + 1) photon scheme at 203.815 nm ($3p'\,^1F_3 \leftarrow 2p'\,^1D_2$), whereas the $O(^3P)$ ground state was ionized by the resonant (2 + 1) photon processes at 226.06 nm ($3p\,^3P_J \leftarrow 2p\,^3P_1$) [13] and at 200.64 nm ($4p\,^3P_J \leftarrow 2p\,^3P_2$). The ions produced by the probe laser are extracted into an ion time-of-flight (TOF) tube before being counted. The delay between the firing of the photodesorption and the probe laser may be changed to obtain a TOF of the photoproducts.

Special care must be taken in the analysis of the data to separate two distinct photoinduced surface processes that lead to the detection of O atoms. In the most drastic process, O atoms are ballistically ejected by the photoinduced dissociation of adsorbed N_2O. In the other process, N_2O itself is photodesorbed from the surface [14,15] and O atoms are subsequently produced by probe laser photolysis of the gas phase N_2O. The photolysis of N_2O near 200 nm produces almost exclusively excited $O(^1D)$ atoms and ground state N_2 molecules [6,7]. The "neutral TOF" profiles of oxygen photofragments are shown in Fig. 1. These TOF profiles reflect the velocity of the neutral fragments coming from the surface. The data shown by the squares were obtained by tuning the probe laser to the $O(^1D)$ resonant transition. Most

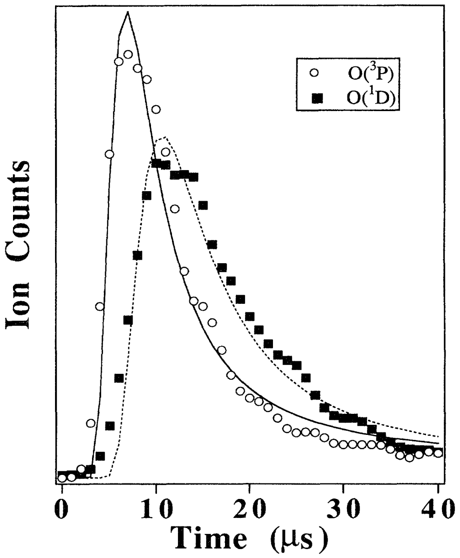

FIG. 1. Raw TOF of neutrals measured at the surface normal. The TOF of ballistic O(^3P) (average kinetic energy = 0.5 eV) is shown as open circles. Most, but not all, of the slower O(^1D) signals, filled squares, come from the gas phase photolysis of photodesorbed N_2O. The lines are fits to a modified Maxwell-Boltzmann function [15].

of the detected O(^1D) in this neutral TOF is not from ballistic oxygen atoms but instead from the photolysis of photodesorbed gas phase N_2O, since rotationally excited N_2, the other fragment of the photolysis [7], has a TOF identical to that of the O(^1D) fragment. We explain later how the nearly field-free ion TOF technique confirms that photodesorbed N_2O molecules are responsible for most, but not all, of the O(^1D) detected by the probe laser.

The TOF of the O(^3P) fragments, shown as circles in Fig. 1, is undoubtedly from ballistic oxygen atoms ejected directly from the surface. The flux weighted average energy of the ballistic O(^3P) is 0.5 eV. Unlike the O(^1D) case, we have been unable to detect N_2 fragments whose TOF matched that of the O(^3P). Moreover, the dependence of the number of O(^3P) ion signals on the power of the probe laser was found to vary as P^2 as expected for the resonant 2 + 1 atomic oxygen transition. By contrast, the weak spin forbidden production of O(^3P) from the photolysis of gas phase N_2O showed a P^4 power dependence because two photons are required to dissociate the N_2O molecule.

The above results strongly suggest that the O(^3P) signal is from ballistic oxygen. Yet, we cannot exclude at this point the possibility that an electronically excited state of N_2O, photodesorbed from the surface and then photolyzed by the probe laser, might produce the strong O(^3P) signal observed. In order to clearly distinguish between atomic oxygen and oxygen produced by the gas phase photodissociation of N_2O, we use a nearly field-free "ion TOF" technique [7]. The ion detection system is aligned vertically and consists of, from top to bottom, a biased repeller plate and a biased extractor grid followed by a negatively biased 10 cm long ion drift tube at the end of which ions are detected (see Fig. 1 in Ref. [7]). Ions are formed by the focused probe laser in the region between the repeller and the extractor plate. The electric field in this region is sufficiently reduced so that the ion transit time to the detector is significantly affected by the velocity vector of the neutral photofragments.

Four sets of ion TOF profiles are depicted in Fig. 2. In the upper ion TOF, Fig. 2(a), the probe laser is tuned and delayed to monitor O(^3P) atoms believed to be ballistically ejected from the surface. This ion TOF peak is sharp and independent of the probe laser polarization with respect to the ion detection system. This is the behavior expected from photodesorbed atomic species

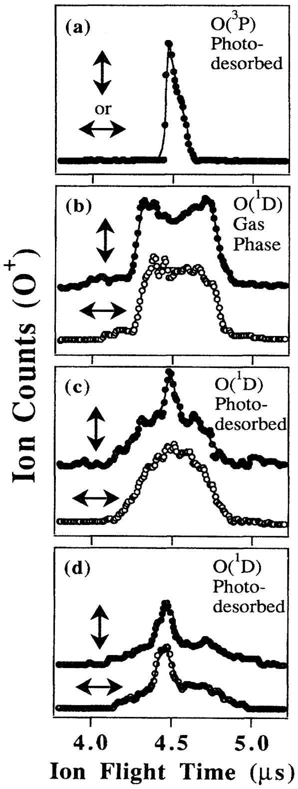

FIG. 2. Nearly field-free TOF of ions from the probe laser ionization point to the ion detector. The arrows indicate the polarization of the probe laser. (a) A sharp ion TOF is produced from ballistic O(^3P) atoms photodesorbed from the N_2O covered surface. (b) O^+ ions produced from the release of O(^1D) in the photolysis of gas phase N_2O. (c) Ion TOF of O(^1D) photoproducts; the sharp feature in the middle (clearer for a vertical polarization) is due to O(^1D) ballistically ejected from the surface, while the rest come from the photolysis of N_2O photodesorbed from the surface. The delay between the photodesorption laser and the probe laser is 8 μs. (d) Same as (c) but for a delay of 5 μs between the photodesorption and probe lasers.

since all the ions formed have nearly the same initial velocity, i.e., the velocity of the neutral atomic species.

The behavior of the ion TOF produced by the photolysis of gas phase N_2O is strikingly different, as can be seen in Fig. 2(b). The photolysis of N_2O is a parallel transition, and the photofragments travel with appreciable velocities along the polarization vector of the probe laser before being ionized [7]. For a vertical polarization, the alignment of the photofragments' initial velocity leads to a very distinct double peak structure as shown in Fig. 2(b). The faster peak is due to photofragments ejected toward the ion detector, and the slower peak is due to fragments initially moving away from the detector. The double peak structure disappears for a horizontal polarization since the photofragments' initial velocity is perpendicular to the ion detection system. The nearly field-free ion TOF technique thus provides a clear method to distinguish between atomic species and photofragments and gives indisputable proof of the photoinduced release of ballistic atomic $O(^3P)$ from the N_2O covered Pt(111) surface.

In Fig. 2(c), the probe laser is tuned to detect $O(^1D)$ from the 193 nm photolysis of the photodesorbed N_2O molecules. For a vertical polarization we observe, in addition to the double peak ion TOF's expected for a probe-induced photolysis, a sharp peak at the center of the signal. This sharp feature is unquestionably due to the presence of electronically excited ballistic $O(^1D)$ released from adsorbed N_2O. The ejection of electronically excited species from metal surfaces seldom occurs since the continuum of states is very efficient at quenching electronic excitations. Figure 2(d) shows that at shorter delays between the photodesorption and probe lasers (5 μs), the sharp feature is enhanced, indicating that the ballistic atomic $O(^1D)$ is faster than the $O(^1D)$ produced by the photolysis of N_2O. From the deconvolution of ion TOF obtained at different delays, we estimate that the kinetic energy of the ballistic $O(^1D)$ is 0.44 ± 0.08 eV, a value similar to the kinetic energy of the ballistic $O(^3P)$ (0.5 eV). The potential energy difference between the ^3P and ^1D states of oxygen is close to 2 eV, and it is remarkable that the two states are observed to photodesorb with roughly the same kinetic energy.

Previous work [12] suggests that on the cold Pt(111) surface, the linear N_2O molecule makes an angle of 35° with the plane of the surface, and thus a tilted lobular angular distribution is expected for the ballistic oxygen atoms. In Fig. 3, the lobular angular distribution of $O(^3P)$ is compared to that of thermalized N_2 molecules desorbing from the same surface in the expected $\cos\theta$ angular distribution [15]. The data were obtained by rotating the focal point of the probe laser about the surface normal. Each data point was obtained by integrating the full TOF of the neutrals and was corrected for the angular variation in ion collection efficiency from measurements of ambient N_2. The TOF profile of ballistic $O(^3P)$ was not found to depend significantly on the desorption angle.

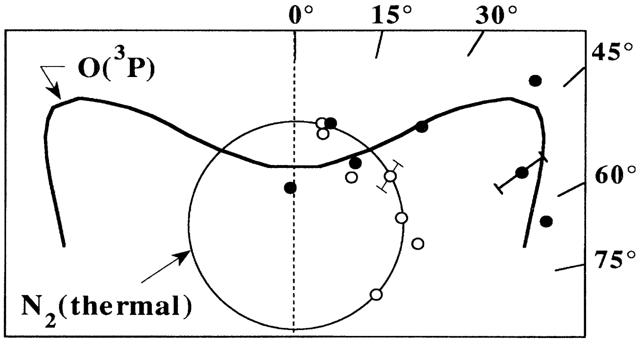

FIG. 3. Angular distribution of photoproducts from N_2O/Pt(111). Filled circles (●) show the ballistic $O(^3P)$ atoms ejected in a lobe tilted along the axis of the adsorbed N_2O. The solid line is a guide to the eye. For comparison, the open circles (○) are from the desorption of thermalized N_2 and follow a $\cos\theta$ (solid line) distribution [15].

Similar information for the ballistic $O(^1D)$ could not be obtained because of geometrical factors which limit the use of the nearly field-free ion TOF technique to a small range of angles. On the Pd(111) surface, O_2 molecules photodesorbed from the α_1 and α_2 states showed no marked translational energy dependence on the desorption angle, while the energy varied with desorption angle for the α_3 binding state [16]. The measured angular distribution of $O(^3P)$ from the surface shows a clear propensity for ejecting the oxygen atoms along the suggested surface bonding angle of N_2O.

By changing the polarization geometry (p vs s) of the photodesorbing laser, it is possible to distinguish between two classes of photoinduced dissociation processes at the surface: direct adsorbate absorption and hot carrier-mediated dissociation [17,18]. In a direct absorption process, the photofragments yield depends on $\boldsymbol{\mu} \cdot \mathbf{E}$, the product of the molecule's dipole moment with the photon's electric field vector [19,20]. We have calculated that for a tilted N_2O adsorbate on the sixfold Pt(111) surface, the averaged $\boldsymbol{\mu} \cdot \mathbf{E}$ product is roughly independent of the polarization geometry at glancing incidence angle [15]. In the second class of processes, the dissociation is triggered by adsorbate interactions with hot carriers which are short-lived energetic electrons or holes excited in the near surface region by the photodesorption laser. At glancing incidence angle, p-polarized light is more efficiently absorbed than s-polarized light by the surface, and a substantial difference in the photoyield is expected for hot carrier mechanisms. We have observed that the yield of ballistic $O(^3P)$ decreased significantly in going from a p to an s polarized geometry, in quantitative agreement with a hot carrier-mediated process [15].

The similar velocities observed for the ballistic $O(^3P)$ and $O(^1D)$ photofragments give an important clue to the nature of the dissociative mechanism. In models of hot carrier-mediated chemistry at surfaces [21,22], the kinetic energy of the desorbates or fragments depends on the amount of time the adsorbate spent in the excited state "N_2O^*." A reasonable explanation for the similar kinetic energies observed for both $O(^3P)$ and $O(^1D)$ is to assume that most of the photofragments' kinetic energy is acquired while the N_2O is in an excited state and that both (O^3P) and $O(^1D)$ are subsequently formed by the eventual decay of the N_2O^*. Comparison with gas phase N_2O data suggests two possible types of dissociative excited states. The promotion of electrons to antibonding orbitals of the adsorbate leads to a neutral unstable state like the bent $2^1A'(B^1\Delta)$ state involved in the gas phase photolysis of N_2O [7]. In this case, the proximity of the metal surface could quench the excited $O(^1D)$ to the $O(^3P)$ state at some point during the dissociation. Note that the kinetic energy of $O(^1D)$ produced by the gas phase photolysis of N_2O at 202 nm is 0.67 ± 0.06 eV [7] in rough agreement with the values found for the photodesorbed $O(^3P)$ and $O(^1D)$. A very different mechanism is suggested by the gas phase dissociation of N_2O by low energy (0–4 eV) electron attachment into N_2 and O^- [8]. Here the extra electron of the ejected O^- ion would have to transfer back to the metal surface, leaving the oxygen atom in either the $O(^3P)$ or the $O(^1D)$ state, both with approximately the same velocity. The kinetic energy of the O^- ion produced by the gas phase electron-induced dissociation of N_2O is 0.4 ± 0.2 eV. Recent calculations show that image charge effects that could reduce the escape velocity of ions from the surface can be small [23] so that the energy of the O^- fragment from the surface may be similar to that observed in the gas phase. Thus, the ballistic $O(^3P)$ and $O(^1D)$ atoms are ejected with similar kinetic energy because they are formed from the same transient surface state: N_2O^* or N_2O^-.

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