Direct Observation of an Intermediate State for a Surface Photochemical Reaction Initiated by Hot Electron Transfer

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The photoinduced charge transfer that had been suggested to result in the dissociation of phenol on Ag(111) was investigated by two-photon photoemission spectroscopy. An unoccupied intermediate state was positively identified, which was found to be located 3.22 eV above the Fermi level. From the photoelectron energy dispersion, the effective mass of the intermediate state was determined to be $(15 \pm 10)m_e$ for a 1 ML coverage of phenol. This implies that the excited electron is localized mainly on the adsorbed phenol, forming a molecular resonance state. Polarization dependence of the photoelectron intensity suggested that the initial photoexcitation of the substrate produces hot electrons that scatter into the molecular resonance state, leading ultimately to the dissociation of the adsorbate. These results are the first two-photon photoemission study to characterize the transient anionic state involved in photodissociation of a molecule adsorbed on a metal surface.

Introduction

Low-energy electrons can be considered one of the simplest but most powerful chemicals ever found. Secondary electrons produced by high-energy radiations are known to be more toxic to living cells than the radiations themselves.[1] Thin DNA films were shown to suffer from single- and double-strand breaks when irradiated with 0–20 eV electrons in an ultrahigh vacuum (UHV) environment.[2,3] Solvated electrons generated by photolysis or radiolysis are known to decompose stable yet hazardous chemicals such as halocarbons.[4,5] Such reductive dehalogenation employing solvated electrons has already been commercialized to treat chlorofluorocarbons, polychlorinated biphenyls, dioxins, pesticides, etc.[6]

In addition to the electron-driven chemistry itself, electron transfer or transport at solid–organic interfaces has attracted considerable interest from a wide scientific community in recent years. In the field of molecular electronics, molecule–metal electrode contact is a subject of increasing importance,[7,8] since the interfacial electronic coupling governs the electrical conductance.[9,10] Electron or hole injection is a crucial step in the operation of an organic light-emitting diode (OLED), and thus the interfacial electronic structures determining the injection barrier have been extensively investigated and utilized to make better OLEDs.[11] Electrons generated by cosmic rays and trapped in the ice particles of polar stratospheric clouds have been suggested to efficiently decompose chlorofluorocarbons adsorbed on the ice, drastically reducing the Antarctic ozone concentration.[12] Photogenerated electrons have often been invoked to explain photodissociation of molecules adsorbed on metal and semiconductor surfaces.[13,14]

To investigate the mechanisms for many of the above processes involving the interfacial transfer of electrons, it is highly desirable to be able to generate an electron packet that is energetically and temporally well-defined and to follow its course in real time. For this, photoexcited electrons generated from a metal substrate by an ultrashort laser pulse have often been used. In surface photochemistry, such processes are modeled by the "hot-electron-mediated" (or indirect excitation) mechanism, where the electron in the substrate metal is excited and transferred to the adsorbate to form a transient anion that leads ultimately to desorption or dissociation.[13–16] While the molecular adsorbate may also be directly excited by the incident photon without much regard to the presence of the metallic substrate underneath,[13] it is widely believed that most photochemistry of adsorbates on metals occurs through the indirect excitation mechanism because photogeneration of charge carriers is in general highly efficient.[17] This hot-electron-mediated mechanism is supported by numerous examples that showed correlations between photoyield and substrate absorbance as a function of the polarization or incidence angle.[13,17,18] As the most direct evidence, anionic photofragments were found to desorb during photoirradiation.[14] Quite surprisingly, however, the transient anion state has rarely been characterized in connection with photochemistry since most studies have so far been concerned with the final reaction products only. Therefore, the study on photoexcited hot electrons is in great demand to understand the electron–molecule interaction on metals and to unravel its implication in surface photochemistry.

In this regard, two-photon photoemission (2PPE) spectroscopy is particularly well-suited to address the issues of surface photochemistry involving hot electrons. In 2PPE, the first photon excites an electron from an occupied substrate band to an unoccupied interfacial state of the adsorbate or the substrate, and then the second photon is used to eject the electron above the vacuum level. With this technique, the photoexcited transient interfacial state can be investigated if the affinity level of the adsorbate lies energetically within access of the pump photon. In the past two decades, 2PPE spectroscopy has been largely employed to investigate the energetics and dynamics of image potential states on various bare and adsorbate-covered metal surfaces.[19] Aromatic molecules have been found to develop an anionic molecular resonance (MR) state delocalized along the surface.[20,21] On the other hand, alkanes and polar molecules were found to trap and localize excess electrons by the formation of small polarons[22] and through solvation,[23,24] respectively. 2PPE can also be carried out in a time-resolved manner, as in the

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14482 *J. Phys. Chem. B, Vol. 109, No. 30, 2005*

Lee et al.

recent elegant femtosecond real-time 2PPE experiment that revealed the nuclear motion of a strongly bound atomic adsorbate.[25]

In this paper, we report direct observation by 2PPE of the unoccupied state of adsorbed phenol on Ag(111) that leads to photodissociation. An adsorbate-induced MR state was found at 3.22 eV above the Fermi level with a considerable degree of spatial localization. Adsorbed phenol has shown intriguing photodissociation behavior on Ag(111) in our previous studies,[26,27] from which a model system was derived for hot-electron-mediated photodissociation. To our knowledge, this constitutes the first direct experimental observation of an MR state for hot electrons that leads to a chemical reaction.

Experimental Section

The experiment was carried out in a UHV chamber, the details of which have been described elsewhere.[27] Only a brief overview with details of the light source and modifications made for this experiment is given here. The UHV chamber is equipped with standard surface science tools, and the base pressure was maintained below 2×10^{-10} Torr during experiments. A laser drilled-pinhole (15 μm diameter) doser with a Baratron gauge (MKS) replaced the leak valve doser to control coverage within a few percent of 1 monolayer (ML). As a light source, we used a tunable dye laser (Spectra-Physics, PDL-3) pumped by a Q-switched Nd:YAG laser (Continuum, Surelite). The UV pump light ($h\nu_1$) was obtained by frequency-doubling the visible probe light ($h\nu_2$) from the dye laser with a BBO crystal. The visible photon energy was varied between 1.7 and 2.0 eV. Both beams were collinearly combined by a dichroic mirror and irradiated the Ag(111) surface at an incidence angle of 67° from the surface normal for dispersion measurement and 45° otherwise. Except for polarization dependence measurements, both beams were p-polarized to make both σ- and π-transitions allowed. Photoelectrons were detected with an electron time-of-flight (TOF) spectrometer that was 32 cm long and surrounded by a magnetic shield. The acceptance angle of the TOF spectrometer was about 4.4°. The TOF of the photoelectrons was recorded with a multichannel scaler (FAST ComTec, P7886) with a minimum temporal resolution of 500 ps. A typical energy resolution was 22 meV at a kinetic energy of 1 eV. The Ag(111) crystal was cleaned by the standard procedure.[27] Phenol (Merck, >99.8%) was purified by several freeze−pump−thaw cycles and dosed to the crystal maintained at 163 K through the pinhole doser. All 2PPE spectra of this paper were taken at a sample temperature of 100 K.

Results and Discussion

The adsorption and photochemical behavior of phenol on Ag(111) have been reported in our earlier papers.[26,27] Briefly, phenol forms three distinct adsorption layers on Ag(111): a weakly chemisorbed layer, an intermediate layer, and an infinitely growing multilayer. The chemisorption layer desorbs molecularly at 250 K with an activation energy of 15 ± 0.5 kcal/mol, which is even smaller than the enthalpy of sublimation of phenol, suggesting a rather weak metal−molecule interaction. When irradiated by an ultraviolet light, however, the adsorbed phenol undergoes hot-electron-mediated photodissociation as shown in Scheme 1. This proposition was supported by two unique observations, one of which is that molecular hydrogen evolved during irradiation, confirming the cleavage of the O−H bond and the subsequent recombination of the resulting hydrogen atoms (Scheme 1b).[26] The other is that a significant amount of phenol desorbed at higher temperatures after irradiation, implying recombinative desorption (Scheme 1d) of the adsorbed

SCHEME 1: Hot-Electron-Mediated Photodissociation of Phenol on Ag(111)
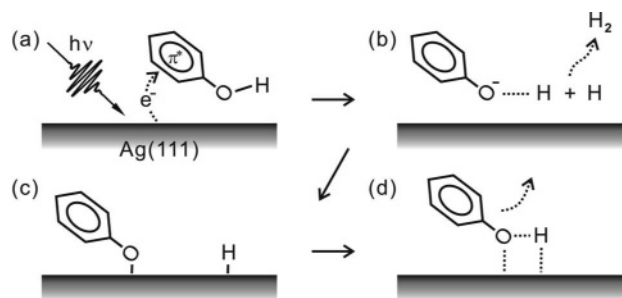
phenoxy and hydrogen atom (Scheme 1c).[27] The photogenerated hot electrons were suggested to scatter into the electron affinity level derived from the lowest unoccupied molecular orbital (LUMO) of phenol. Since this transient anion state was believed to be the intermediate species for the dissociation reaction and such an observation has not been reported in the literature, we set out to perform a 2PPE experiment on this intriguing system.

Figure 1 shows a series of 2PPE spectra for phenol adsorbed on Ag(111) for coverages (Θ) up to 1 ML. The coverage in this range was controlled by varying the substrate temperature over 200−260 K after dosing an excess amount of phenol. The coverage was determined from the integrated area of the thermal desorption peak. At a very low coverage, there appear a broad secondary electron band with an edge (E_{vac}) at 4.4 eV and a sharp, intense peak at 5.7 eV that originates from resonant excitation of the surface state to the image potential (IP) state at $n = 1$. As the coverage increases, another broad band (designated MR for molecular resonance state) emerges to become a main feature, which is apparently associated with the
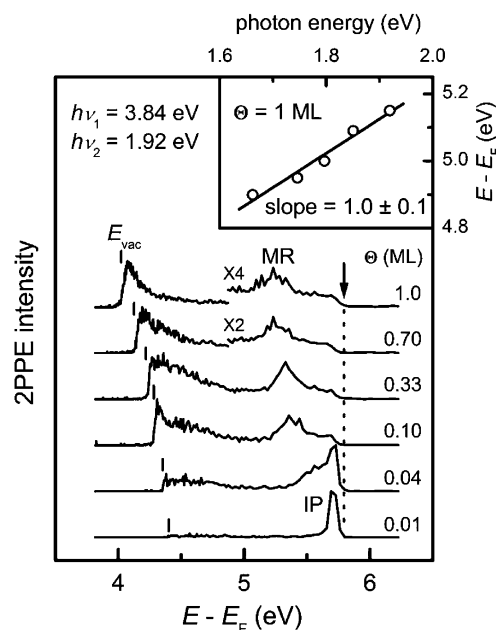

Figure 1. 2PPE spectra of phenol/Ag(111) in normal emission at various coverages (Θ). The spectra are shown as a function of the final state energy $E - E_F = E_{kin} + \Phi$, where E_F, E_{kin}, and Φ are respectively the Fermi energy, the electron kinetic energy, and the work function. E_{vac} at the edge of the secondary electron band represents the vacuum energy from the Fermi level, i.e., the work function Φ. The arrow and dotted line represent the sum of the photon energies, $h\nu_1 + h\nu_2$. "IP" and "MR" stand for the image potential state and the molecular resonance state, respectively. The inset shows the photon energy dependence of the MR band energy at $\Theta = 1$ ML. The visible photon energy ($h\nu_2$) was varied from 1.66 to 1.92 eV.
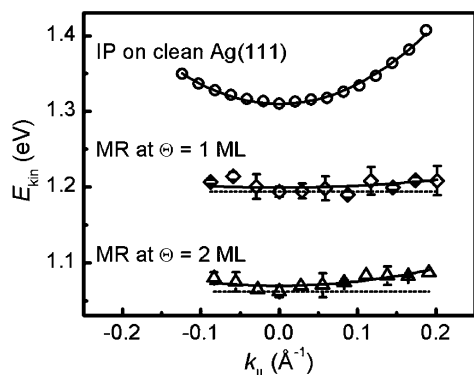
Surface Reaction Initiated by Hot Electron Transfer

J. Phys. Chem. B, Vol. 109, No. 30, 2005 **14483**

Figure 2. Dispersion of electron kinetic energy from intermediate state obtained by angle-resolved 2PPE spectroscopy at different coverages specified. Since the difference in contact potential between the surface and the detector was set to zero, E_{kin} is referenced to the vacuum level. The probe energy $h\nu_2$ was 2.06 and 1.75 eV for the IP state and the MR state, respectively. Solid lines are parabolic fits to the data, while dotted lines represent hypothetical nondispersive states drawn for comparison.
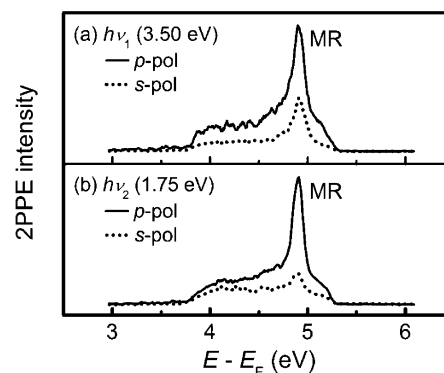

Figure 3. Polarization-dependent 2PPE spectra for phenol/Ag(111) at 2 ML. (a) The probe photon $h\nu_2$ was fixed p-polarized while the pump photon $h\nu_1$ was p- (solid line) and s-polarized (dotted line). (b) The pump photon $h\nu_1$ was fixed p-polarized while the probe photon $h\nu_2$ was p- (solid line) and s-polarized (dotted line).

adsorbed phenol. At coverages higher than 0.1 ML, the IP peak virtually disappears as the secondary electron band and the MR band become more prominent. The plot in the inset of Figure 1 shows how the peak position of the MR band at 1 ML changes as the photon energy is varied. The linear relationship with a slope of 1.0 ± 0.1 indicates that the origin of the MR state is an unoccupied intermediate state.[19] The energy of the MR state can be obtained by subtracting the second photon energy ($h\nu_2$) from the final state energy ($E - E_F = E_{kin} + \Phi$), which comes out to be ca. 3.22 ± 0.02 eV above the Fermi level. Note that the intermediate state moves toward the Fermi level in parallel with E_{vac} as the coverage increases.

The UV photon used in 2PPE can induce charge transfer that could ultimately lead to photodissociation if the unoccupied intermediate state is resonant in energy with the hot electron produced by photoexcitation. Indeed, a small amount of phenol was found to undergo photodissociation even though the light intensity was kept as low as possible. It should be noted, however, that the adsorbate-induced spectral feature in Figure 1 comes from phenol itself rather than its dissociation product, which in this case would be the adsorbed phenoxy. Upon removal of the intact phenol by thermal desorption to 260 K, the adsorbate-induced band disappears completely and the 2PPE spectrum becomes virtually identical with that for clean Ag(111). In a control experiment, we found that the 2PPE spectrum obtained after the UV irradiation (266 nm) that dissociates more than 30% of the adsorbate remained unchanged from the one obtained before such irradiation. These results indicate that the MR band comes from the adsorbate in its original, undissociated form. The fact that a molecular resonance for phenoxy was not observed, however, should not rule out the existence of such a resonance because the current control experiment cannot prepare a sole layer of phenoxy, which is beyond the scope of our work.

Figure 2 shows the dispersion of electron kinetic energy along the surface parallel, obtained by angle-resolved 2PPE measurement at different coverages. The result refers to the IP state of Ag(111) at $\Theta = 0$ and the MR state of phenol/Ag(111) otherwise. The effective mass of the electron, m_{eff}, in the photoemission state can be determined by fitting the data to the parabolic equation $E_{kin} = E_0 + (\hbar k_\parallel)^2/2m_{eff}$, where $\hbar k_\parallel$ is the surface parallel momentum. The effective mass of the IP state on clean Ag(111) was determined to be $(1.44 \pm 0.04)m_e$ (m_e = free electron mass), which agrees well with the reported values.[28,29] On the other hand, the MR state at 1 ML has an

effective mass of $(15 \pm 10)m_e$, where the rather large uncertainty is due to the broadness of the MR band and the reciprocal relation between the effective mass and energy dispersion.[30] Despite the uncertainty, the nonzero dispersion of the MR state is evident at higher parallel momentum in Figure 2. Such a large effective mass suggests that the MR band originates from a mildly localized molecule-derived state, whose occupation endows the adsorbate with an anionic character that may lead to dissociation. When the coverage is increased to 2 ML, the effective mass is decreased to $(6.8 \pm 1.5)m_e$, indicating a higher degree of dispersion. This might be explained by the formation of loosely coupled bands among the adsorbates at a higher coverage that enables the electron to move more freely, as has been observed in the case of C_6F_6/Cu(111).[21] Although several molecular systems have so far exhibited a certain degree of electron localization,[22-24] a large effective mass such as has been observed in our study is a striking result, which has never been reported to date for aromatic compounds.

A detailed excitation mechanism for individual steps of the 2PPE process can be investigated by studying the polarization dependence of the 2PPE signal.[31] To examine the first (photo-excitation) step of 2PPE, we fixed the visible light to be p-polarized and employed a p- and s-polarized UV light to obtain the two photoelectron spectra shown in Figure 3a. The MR band with the p-polarized pump has an intensity considerably higher than that with the s-polarized pump, but the latter also has a significant intensity itself. This suggests that the photoexcitation is of a mixed character in σ/π-symmetry. On the other hand, in the second (photoemission) step of 2PPE, the transition from the MR state to a final state above the vacuum level is strongly forbidden for the s-polarized visible light as evidenced by its small intensity (Figure 3b), indicating that the transition dipole moment is oriented mainly along the surface normal (σ-symmetry) in the photoemission step.

Regarding the first step, we note that the intensity ratio of the peaks in Figure 3a is quite close to the absorptance ratio $A_{s-pol}/A_{p-pol} = 54\%$ of silver surface at the employed photon energy of $h\nu_1$, where $A_{p-pol} = (1 - |r_p|^2)$, $A_{s-pol} = (1 - |r_s|^2)$, and r_p and r_s represent the Fresnel reflection coefficients for p- and s-polarized light, respectively.[31] The complex refractive index at $h\nu = 3.49$ eV is $0.209 + 1.44i$ [32] at an incidence angle of 45°. Notably, the intensity ratio of the secondary electron band between the s- and p-polarized pump turns out to be nearly equal that of the MR state band. Although we cannot rule out direct excitation of mixed character in σ/π-symmetry, the good correlation between the absorbance and 2PPE intensity of the
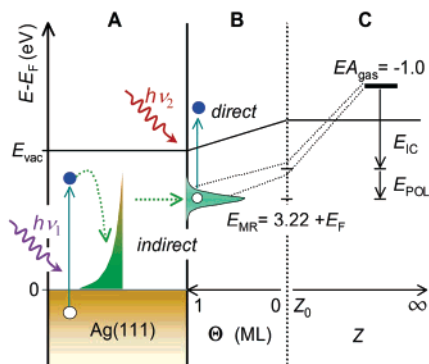
Figure 4. Schematic diagram of the hot-electron-mediated mechanism. In column A, a cascade of hot electrons generated by the pump photon $h\nu_1$ scatter into the anionic MR state ("indirect" excitation). Before undergoing relaxation, the electron in the transient anion is ejected by the probe photon $h\nu_2$ ("direct" transition of σ-symmetry, column B). In column C, the energetics of the adsorbate system is shown as a crude function of the distance Z from the substrate: adsorption brings down the electron affinity level in the gas phase (EA_{gas}) by an amount E_{IC} via ion−image charge interaction. Upon increasing the coverage, the energy of the MR state, E_{MR} is further lowered toward the Fermi level by E_{POL} due to the polarization interaction between the anionic adsorbate and its surrounding neighbors as indicated in column B.

MR band or secondary electron band suggests that the MR state is excited by transfer of the photoexcited secondary electrons[31] as in the hot-electron-mediated surface photochemistry.[13,17,18] A similar indirect excitation pathway with direct dependence on the substrate absorptance was observed for the σ-state of CO/Cu(111), where the secondary electrons were generated from high-lying d-band excitations.[31] We conclude that the present result provides direct evidence, for the first time by 2PPE, for a chemical change brought about by the hot-electron-mediated mechanism, which has been anticipated but not observed to date.[33,34]

The energy of the MR state is in accord with the estimated threshold energy of photodissociation, 3.2 eV, from our earlier work.[27] In terms of the hot-electron-mediated mechanism, the energetic electrons generated by the UV pump ($h\nu_1$) tunnel into the MR state located at 3.22 eV above the Fermi level as described schematically in Figure 4. The resulting transient anion is to undergo relaxation by transferring the excess electron back to the substrate or dissociate into phenoxy radical anion and hydrogen atom. In 2PPE, however, the electron in the transient anion is ejected by the visible probe ($h\nu_2$) before undergoing relaxation or dissociation. The photoelectron thus contains information on the MR state. Although we do not know the exact identity of the electronic state responsible for the MR state, the π^* a_2 state of phenol is a likely candidate because it is the lowest anionic resonance state with an electron affinity of -1.0 eV.[35] As the distance Z between the surface and the molecule decreases to Z_0 upon adsorption, the anionic resonance state is greatly stabilized due to the image charge interaction, as represented by the image charge stabilization energy E_{IC} in column C of Figure 4. As the coverage increases, the polarization interaction between the anion and its surrounding neighbors can further stabilize the anionic state by the polarization stabilization energy E_{POL}, as shown in column B of Figure 4.[20,36] Since the binding energy of the MR state at 1 ML is calculated to be $E_{vac} - E_{MR} = 3.95$ eV $- 3.22$ eV $= 0.73$ eV, the total stabilization energy amounts to 1.7 eV, which is quite consistent with the estimation based on simple electrostatic considerations.[27] The dramatic increase in photodissociation cross section with increasing coverage experimentally observed in the previous work[27] agrees well with the coverage-dependent polarization stabilization.

The present 2PPE study has identified the transient anionic state responsible for the hot-electron-mediated surface photochemistry suggested from our earlier work. Specifically, we determined the energy of the anionic state and validated the excitation mechanism, both of which are rarely addressed directly by conventional surface science techniques. For complete understanding of the phenomenon, however, further studies are necessary. For instance, the observed effective mass, which is unusually high but far from infinity, deserves further investigation to see if any nuclear motions are involved in the apparent electron localization and thus to identify the exact nature of the transient anion state. On the other hand, time-resolved 2PPE may be employed to track the dissociation of the transient anion, as has been done for photodesorption of Cs on Cu(111).[25]

Conclusion

We have observed for the first time by 2PPE an adsorbate-derived unoccupied molecular state that leads to a photochemical reaction on a metal surface. We found that the MR state is spatially rather localized around the adsorbate molecule. The photoexcited electrons are transferred to the MR state by the hot-electron-mediated mechanism. The energy of the MR state and its coverage dependence agree well with the results of earlier surface photochemical studies. A femtosecond time-resolved study is in progress to address dynamic issues related to the current problem and to shed more light on its surface photochemistry.

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Surface Reaction Initiated by Hot Electron Transfer

J. Phys. Chem. B, Vol. 109, No. 30, 2005 **14485**

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