Direct Evidence for Charge-Transfer Photodissociation at a Metal Surface: $CCl_4/Ag(111)$

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Observation of negative ions desorbing from an adsorbate-covered metal surface following UV laser irradiation gives direct evidence that the mechanism responsible is charge-transfer photodissociation (CT-PDIS). We have studied photoemission of ions for $CCl_4/Ag(111)+h\nu \rightarrow Cl^-(g)+CCl_3/Ag(111)$. The CT-PDIS mechanism is supported by comparison of the yield of desorbing Cl^- and photoemitted electrons with the variation in UV photon energy and surface coverage. Charge transfer leading to negative-ion emission is also shown to occur in the absence of photoelectron emission (i.e., $h\nu < \phi$) for $CCl_4/Ag(111)$.

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The photochemistry of molecules adsorbed at surfaces has been an area of recent experimental activity [1]. In many cases, photodissociation of the adsorbate, PDIS, is due to direct absorption of a UV photon. In other cases, enhancement of the cross section for PDIS has led to proposals for indirect excitation by way of the substrate, either through electronic-to-electronic energy exchange from substrate to adsorbate [2], or by charge transfer (CT) [3-8]. The second of these mechanisms, charge-transfer photodissociation, CT-PDIS, should lead to the formation of anionic photofragments, but these have not been detected previously. In the present study we report the detection of Cl^- anions leaving the surface, thus providing direct evidence for the CT-PDIS mechanism in $CCl_4/Ag(111)$. We have obtained the yield of Cl^-, and also of photoemitted electrons, as a function of photon energy and adsorbate coverage.

The experiments were performed in a UHV chamber described previously [9] with a base pressure in the low 10^{-10}-torr range. We have added a home-built time-of-flight (TOF) negative-ion mass spectrometer [6] in order to measure the flux of negative ions desorbing from a surface. This spectrometer consists of ion extraction optics facing the sample, a short flight tube, an electromagnetic deflector (to remove photoelectrons from the ion signal), a microchannel-plate detector (MCP) array, and pulse counting electronics connected to a LeCroy multichannel scaler. The MCP was gated "off" until a few μs after the laser pulse in order to prevent saturation of the detector by photoelectrons. Negatively charged particles arriving at the MCP after the laser fired were counted in 256 1-μs bins. The counts from successive laser shots were summed to give the TOF spectrum. The photoemission of electrons from the Ag(111) crystal was also monitored, using a charge-sensitive preamplifier connected to the sample, so that the electron photoemission could be compared with the negative-ion yield.

The 10-mm-diam polished Ag(111) crystal was cleaned *in situ* by cycles of Ar^+-ion bombardment and annealing, until the Auger electron spectrum showed no traces of contamination. The sample was mounted on a Ta plate with Ta clips, in thermal contact with a liquid-N_2 reservoir. It was electrically isolated by sapphire plates. The sample could be cooled to 100 K, and heated to 800 K by electron bombardment.

Spectroscopic-grade CCl_4 was used in a glass and Teflon gas handling system. The adsorption of CCl_4 on Ag(111) was characterized by temperature programmed desorption (TPD) and Auger spectroscopy. Gas dosing was performed by backfilling the chamber with CCl_4 vapor. The doses quoted were corrected for the ionization-gauge efficiency for CCl_4 (6.0). The occurrence of new desorption peaks in the TPD spectra show that the adsorption of 1 (corrected) langmuir (1 L) of CCl_4 corresponded approximately to the formation of 1 monolayer (1 ML). All of the experiments were performed on an Ag(111) substrate at a temperature of 100 K, at which temperature it is possible to grow multilayers of CCl_4. A fraction of the first monolayer of CCl_4 dissociated upon adsorption to form AgCl and adsorbed chlorocarbons; subsequent CCl_4 dosed in the first and succeeding layers adsorbed molecularly on the surface. The experiments reported here were performed over a range of coverages from 0.2 to 7 layers.

We have used two different laser systems in the experiments reported here. The primary laser was a pulsed excimer laser (Lumonics TE-860) operating at 6.4-, 5.6-, 5.0-, 4.0-, and 3.5-eV photon energies, i.e., 193, 222, 248, 308, and 350 nm, respectively. The laser intensity was attenuated by transmission through dielectric mirrors. In a second set of experiments the UV radiation source was the frequency-doubled output from a yttrium aluminum garnet-pumped dye laser; this gave photons in the range 4.1-5.0 eV, i.e., 250-300 nm. Both the excimer and dye lasers were unfocused, and both were incident upon the sample at 77° to the normal, i.e., grazing incidence.

Figure 1 shows a typical TOF spectrum obtained for negatively charged particles leaving the surface after irradiation by a 6.4-eV (193 nm) UV laser pulse. The prominent peak at $t=30$ μs corresponds in time to the arrival of Cl^- negative ions from the $CCl_4/Ag(111)$ surface. This spectrum was obtained after 640 laser shots from 1 ML of $CCl_4/Ag(111)$ using an incident laser power in the nanojoule region (60 nJ/pulse). A power study has

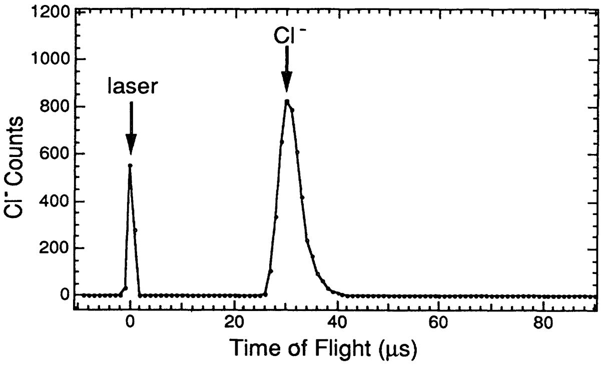

FIG. 1. Typical time-of-flight spectrum obtained from 1 ML of CCl_4/Ag(111) using 193-nm excimer laser radiation. The peak at $t = 30$ μs is caused by the arrival of Cl^- ions formed at the surface.

shown that this ion yield is linear in laser power over the range of low laser fluences used in this work; hence the signal can be attributed to a one-photon process [6].

In order to investigate the mechanism for negative-ion desorption due to UV photon irradiation of the surface, the negative-ion yield from 1 ML CCl_4/Ag(111) was measured as a function of the photon energy. Figure 2 shows the relative yield of Cl^- ions over the range of 3.5–6.4-eV photon energies, using laser fluences of ~1 $\mu J/cm^2$. A small but measurable ion desorption yield begins at $h\nu = 4.1$ eV. The yield increases monotonically as the photon energy is increased. The inset in Fig. 2 shows the photoemission current over the range of photon energies near the threshold for ion desorption. The most important feature of this inset is the observation that the photoemission of electrons from our sample begins at $h\nu = 4.4$ eV; i.e., we are able to observe Cl^- ion desorption from the surface for a range of photon energies, 4.1–4.4 eV, at which there is *no photoelectron emission.*

The desorption of negative-ion fragments from molecules adsorbed on a metal substrate can be understood as follows. The UV photons irradiating the metal surface generate excited photoelectrons within the metal. The continuous density of states for electrons near the Fermi level E_F means that a broad distribution of photoelectron energies can be formed, both above the vacuum level E_{vac} (free electrons) and below E_{vac} ("hot" electrons). These photoelectrons can attach to the adsorbed molecules to form a negative ion if the energy and incident direction of the electron upon a molecule is in the range for a negative-ion resonance [10].

The negative ion at the surface can then either reemit the electron (autodetachment) in an elastic or inelastic process (the latter could involve rotational or vibrational excitation of the adsorbate) or, in the case of CT-PDIS, dissociate the adsorbate to produce one neutral and one negative-ion fragment. In the case of CCl_4, in the gas phase a resonance for dissociative electron attachment

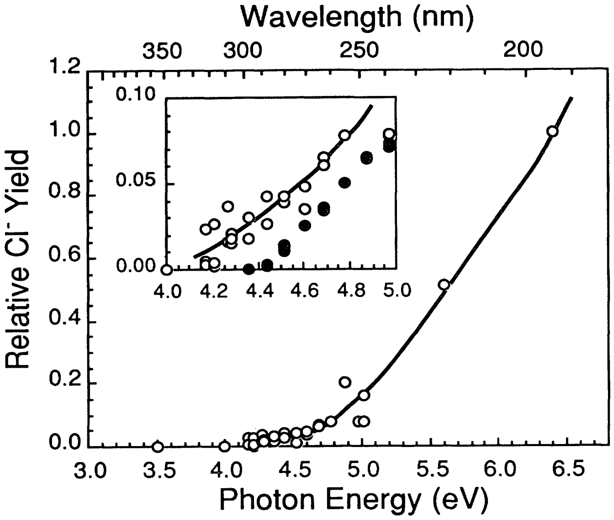

FIG. 2. Yield of Cl^- ions from 1 ML of CCl_4/Ag(111) as the laser photon energy is varied. The data points between 4.1 and 5.0 eV were obtained using tunable UV laser radiation while the other points were obtained using excimer laser transitions. Inset: The measured negative-ion (open circles) and photoelectron (solid circles) emission from the sample near the threshold region.

(DA) forming Cl^- is located at very low incident electron energy (peaking near 0 eV) with a large cross section [11,12]. This DA process for CCl_4 can be summarized as

$$e^- + CCl_4 \rightarrow [CCl_4^-]^\ddagger \rightarrow CCl_3 + Cl^- \qquad (1)$$

in which the double dagger indicates a transition state. Charge-transfer photodissociation of CCl_4 would therefore be expected to require a photoelectron of the correct (low) energy to be captured by the adsorbed molecule.

In the context of these experiments there is a further energy requirement in order that the ions can escape from the metal surface, due to the presence of an image potential for charged particles. This lowers the energy for the charged particles. The maximum energy of a desorbing negative ion from a metal surface after CT-PDIS can be estimated from kinematic and energetic considerations as follows:

$$E_{max} = (1-\beta)\{h\nu - \phi + V_{im} - \Delta + A\} - V_{im}, \qquad (2)$$

where β is the ratio of the ion to the molecular mass, ϕ is the surface work function, V_{im} is the image potential energy at the position of the adsorbed molecule, Δ is the dissociation energy of the bond in the neutral molecule that is being broken and A is the electron affinity of the desorbing ion. Using values of these parameters from gas-phase and surface data ($\phi = 4.46$ eV [13], $V_{im} = 1$ eV [14], $\beta \approx 0.23$, $\Delta = 3.06$ eV, and $A = 3.61$ eV [15]), Eq. (2) can be used to predict the minimum photon energy for negative-ion desorption, corresponding to $E_{max} = 0$.

For the above parameters we find a minimum photon energy of $h\nu_0 = 4.2$ eV. This cutoff photon energy is roughly 0.3 eV below the surface work function used in (2) and is consistent with our independent observation of negative-ion desorption at photon energies below that for which electron photoemission can be observed. We have used the work-function value for clean Ag(111) in (2) because the onset of electron photoemission (inset, Fig. 2) occurred close to the value for clean Ag(111). Emission of Cl^- ions at photon energies below the work function occurs in the present case because of the exothermicity of reaction (1) and the presence of hot electrons. This charge transfer from metal to adsorbate without the formation of free electrons is commonly described as tunneling. Evidence for tunneling in CT-PDIS has been previously obtained in a number of laboratories, in a less direct fashion [4-7].

The dependence of the Cl^- yield on CCl_4 coverage is shown in Fig. 3. The coverage dependence was obtained using 6.4-eV (193 nm) photons and 60-nJ energy per laser pulse. The CCl_4 was deposited sequentially in small doses after measuring the yield at each point. The Cl^- ion yield was found to peak very sharply at 2-L (roughly 2 ML) surface coverage and then to decrease steeply. By 5-L coverage the signal had been attenuated to only ~3% of the peak value.

The corresponding electron photoemission from the surface is also shown in Fig. 3. In contrast to the Cl^- ion signal, the electron photoemission signal decreased gradually and monotonically from the clean-surface value. At 5 L the electron emission had only decreased to ~50% of its initial value. Qualitatively, the ion yield would be expected to increase with CCl_4 adsorption at low coverage due to the presence of more molecular CCl_4 in the first layers and then decrease for multilayer coverage of CCl_4 because the electrons are unable to reach the top layer. Charge-transfer photodissociation can occur for the molecules close to the metal surface, but the ions produced there cannot escape to our detector since they are trapped by the molecular layers adsorbed above.

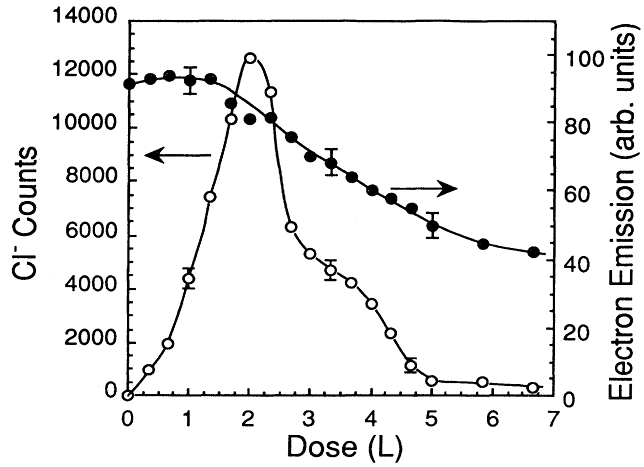

FIG. 3. Coverage dependence of the Cl^- yield (open circles) and electron photoemission (solid circles) from the sample as a function of the CCl_4 dose.

The pronounced decrease in negative-ion yield that occurred despite the fact that the electron photoemission yield had decreased only modestly could be due to the selective removal of the majority of the photoelectrons of the appropriate low energy to cause DA of CCl_4(ad) [16]. The total electron-scattering cross section for gas-phase CCl_4 at energies near the peak for DA is very large [12], so scattering in the CCl_4 solid should be effective in removing electrons of ~0 eV from the initial energy distribution.

The "kink" in the Cl^- yield curve from 3-4 L (Fig. 3) may be caused by the changing structure of the adsorbed layers. The probability of a Cl^- product ion escaping its image potential is markedly sensitive to its direction of motion relative to the surface normal. For an ion of given energy at a metal surface, there is a restricted "cone of escape" from the surface [17]. If the dissociating bond direction, and hence ejection direction, is too far from the surface normal, the image potential will cause the ion to arc back to the surface. The additional contribution to the Cl^- yield curve at 3-4-L coverage (the kink) could be related to realignment of the C-Cl bond directions with respect to the surface normal. Structural changes are commonly observed as adlayers begin to form more bulklike structures at multilayer coverages [18].

Although only a small fraction of the Cl^- produced at the surface escapes to our detector, we have estimated the quantum efficiency of CT-PDIS per incident photon as $\sim 1\times10^{-4}$ by Auger measurement of the rate of chlorination of the Ag(111) surface with a 2-L CCl_4 dose at a photon energy of 6.4 eV. A loss of $\sim 10^{-1}$ would be expected due to the reflectivity at grazing incidence and a further loss of $\sim 10^{-3}$ due to the low conversion efficiency of light into photoelectrons [19]—consequently a quantum efficiency of $\sim 1\times10^{-4}$ would be consistent with DA in the region of unit efficiency.

We report observations of the desorption of negative ions following UV laser irradiation of an adsorbate-covered metal surface. The mechanism responsible for this effect has been demonstrated to be charge-transfer photodissociation, in which photoemitted electrons or hot electrons within the metal dissociatively attach to the adsorbed molecules causing a rupture of one of the bonds and emission of a negative ion. The wavelength and coverage dependence of the Cl^- ion yield from the CCl_4/Ag(111) adsorption system shows the role of free and hot photoelectrons in CT-PDIS.

In an extension of these experiments we have deposited a variable thickness of CH_3X (X=Br,I) over the CCl_4 adsorbate (1-10 ML). It was found that Cl^- could be efficiently converted to CH_3Cl in the ion-molecule reaction $Cl^- + CH_3X(ad) \rightarrow CH_3Cl(ad) + X^-$, as determined by TPD after irradiation [20].

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