Alkali Promotion of Photodissociation of Adsorbed $Mo(CO)_6$

Z. C. Ying and W. Ho

Laboratory of Atomic and Solid State Physics and Materials Science Center, Cornell University, Ithaca, New York 14853-2501

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Coadsorption of potassium is observed to significantly enhance photodissociation of $Mo(CO)_6$ adsorbed on Cu(111) and Si(111)7×7 by opening a completely different photodissociation channel. In addition to the direct photoelectronic excitation of $Mo(CO)_6$ on K-free surfaces, the dominant photodissociation process on K-coadsorbed surfaces involves attachment of photogenerated hot electrons to the adsorbate, which is energetically possible due to substantial decreases in the work function.

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The presence of a substrate is known to exert significant effects on the photoreactions of adsorbed molecules. For example, quenching of photoexcitation by the substrate substantially reduces the photoreaction yield.[1-3] The substrate, under high-power irradiation, can also act as a heat bath, leading to thermal reactions.[1,4,5] Furthermore, substrate photoexcitation can be transferred nonthermally to the adsorbate and introduce novel channels of surface photoreactions.[6-8]

Alkali promotion of thermal reactions of adsorbed molecules has been studied for many years.[9] In the present study, we show for the first time that alkali coadsorption drastically enhances surface photoreaction by creating an additional channel.

Photodissociation of $Mo(CO)_6$ adsorbed at 85 K on clean and potassium-preadsorbed Cu(111) and Si(111)7×7 was studied, with different photon powers (0.5–30 mW/cm^2), wavelengths (250–800 nm), polarizations (s and p), and incident angles (20°–70°). The experiments were performed in a stainless-steel ultrahigh-vacuum chamber.[1,10] The K coverages on Cu(111) and Si(111)-7×7 surfaces were 0.15 and 0.5 monolayer (ML), respectively, and coincided with the maximum decrease in the work functions (-2.6 ± 0.1 eV for both surfaces). The exposure of $Mo(CO)_6$ was 1 L [1 L (langmuir) $=10^{-6}$ Torr s], which corresponds approximately to 1-ML coverage. Xe and Hg-Xe arc lamps (1000 W), in combination with a grating monochromator, provided up to 30 mW/cm^2 radiation with a bandwidth of about 10 nm. Unless otherwise indicated, the incident angle was 40° from the surface normal.

The adsorption of $Mo(CO)_6$ was characterized by high-resolution electron-energy-loss spectroscopy (HREELS) and thermal-desorption (TD) spectroscopy.[1,11] $Mo(CO)_6$ is physisorbed on potassium-free Cu(111) and Si(111)7×7 at 85 K. The energies of the three major vibrational peaks of $Mo(CO)_6$ (Mo-CO stretch, Mo-CO bend, and C-O stretch), observed by HREELS at 46, 74, and 251 meV, are essentially the same as those in the gas and solid phases.[12] The TD temperature of $Mo(CO)_6$ is 200 K, which corresponds to an activation energy of 0.4 eV. On surfaces coadsorbed with K, a small fraction of $Mo(CO)_6$ is decomposed. The TD temperature for the molecularly adsorbed $Mo(CO)_6$ increases slightly to 210 K. The energies of the three major vibrational peaks for molecular $Mo(CO)_6$ are shifted by <2 meV. Furthermore, electronic EELS reveals that the electronic transition energies, intensities, and linewidths of molecular $Mo(CO)_6$ are not significantly perturbed by K.[13]

Two typical photon-induced-desorption (PID) spectra are shown in Fig. 1. When irradiation started at $t=0$ s, the desorption signal was observed at mass 28 (CO) but not at mass 96 (Mo), indicating that the desorbed species was CO and not $Mo(CO)_6$. The PID signal was negligibly small for surfaces dominated by dissociative adsorption.

HREEL and TD spectra recorded after irradiation show diminished intensity for peaks associated with the molecularly adsorbed $Mo(CO)_6$. In addition, new features that can be attributed to carbonyl fragments were observed on the K-free surfaces. The concentration of carbonyl fragments on the K-coadsorbed surfaces was significantly increased after irradiation. It can be concluded that adsorbed $Mo(CO)_6$ molecules photodissoci-

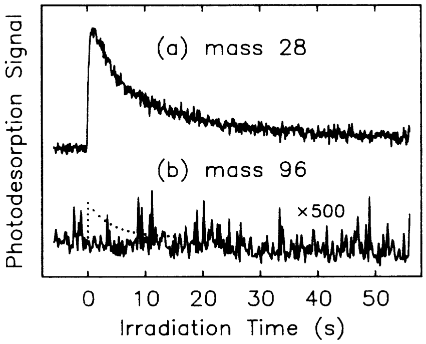

FIG. 1. PID spectra, monitoring masses (a) 28 and (b) 96, for 1-L $Mo(CO)_6$ adsorbed on potassium-preadsorbed Cu(111) at 85 K ($\lambda=436$ nm, $P=12$ mW/cm^2). The dotted line is the expected signal at mass 96 if the desorbed species were $Mo(CO)_6$.

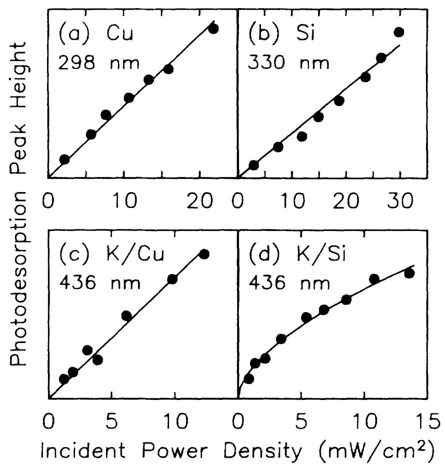

FIG. 2. Peak height of the PID signal vs the incident power density, with the least-squares fits shown by the solid lines. The linear y scale is in arbitrary units for the different panels.

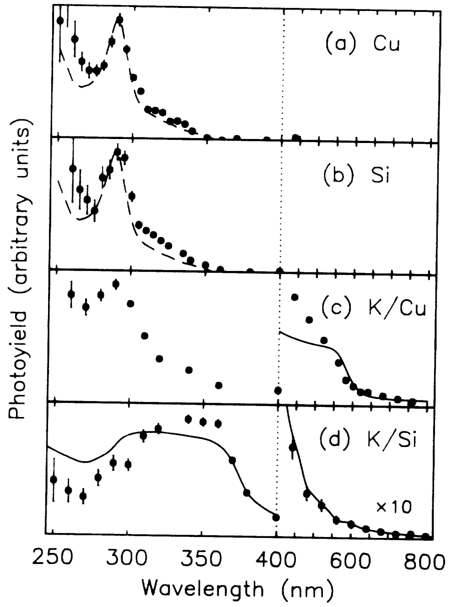

FIG. 3. Wavelength dependences of the photoyield. The linear y scale is in arbitrary units for the different panels. Also note the different x and y scales above 400 nm for each panel. See the text for definition of various lines.

ate into carbonyl fragments and CO, and the product CO desorbs under irradiation. Since the temperature rise under irradiation was measured to be insignificant (< 2 K), the photodissociation is not due to irradiative heating.

In order to determine the mechanisms for the photodissociation of $Mo(CO)_6$, the photoyield was measured as a function of photon power, wavelength, polarization, and incident angle. Figure 2 shows the PID peak height I versus the incident power density P for $Mo(CO)_6$ on Cu, Si, K/Cu, and K/Si. Linear power dependences are observed for these systems except for $Mo(CO)_6$ on K/Si, which exhibits a fractional power dependence, $I \propto P^m$ ($m \approx 0.6$). Shown in Fig. 3 are the wavelength dependences of the photoyield, defined as I/F ($I^{1/m}/F$ for K/Si), where F is the number of incident photons. PID is observed only in the uv region ($\lambda < 360$ nm) for the K-free surfaces. However, with coadsorbed K, the PID signal extends to the visible and near-ir regions and is also increased substantially in the uv [by factors of 2 and 7 at 298 nm for $Mo(CO)_6$ on K/Cu and K/Si compared to Cu and Si, respectively]. The dramatic difference in the wavelength dependence suggests that a new photodissociation channel is opened by coadsorbed K and makes additional contributions to the photoyield. Figure 4 shows the incident-angle dependences of the photoyield ratio between s and p waves, $\gamma I_s/I_p$ [$\gamma(I_s/I_p)^{1/m}$ for K/Si], where $\gamma = F_p/F_s$.

The most likely nonthermal mechanisms for surface photoreactions are (i) electronic excitation of the adsorbate by direct photoexcitation and (ii) attachment of photogenerated hot carriers to the adsorbate. The photoreaction rate due to direct electronic excitation is a function of the electric field of the light wave. Because $Mo(CO)_6$ interacts weakly with the surface, it is assumed that adsorbed $Mo(CO)_6$ mainly retains the O_h symmetry of the free molecule. Therefore, the photoreaction rate is proportional to the square of the amplitude of the electric field and not sensitive to its direction. The macroscopic field[14] is used in the analysis.

In a substrate-mediated photoreaction, electrons and holes are created at a rate of $(1-R)F$, where R is the reflectivity of the substrate. However, only carriers created near the surface can reach the surface and induce reactions of the adsorbate. For simplicity, it is assumed that the carriers created within a distance δ from

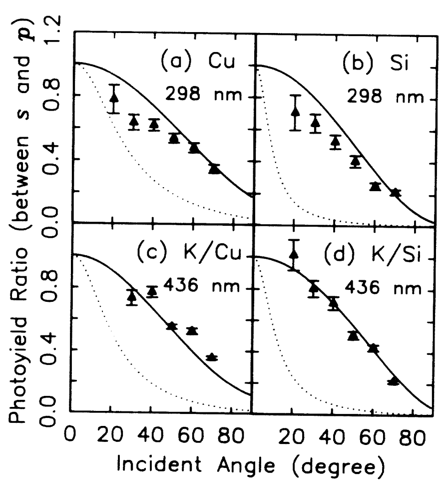

FIG. 4. The photoyield ratio between s and p waves at different incident angles. See the text for definition of various lines. (Both 298 and 436 nm are strong emission lines of the Hg-Xe arc lamp.)

the surface have a constant probability to induce a reaction and those created deeper are not effective. The value of δ is expected to be of the order of 10^{-6} cm (assume 10^{-14}-s lifetime and 10^{8}-cm/s speed for carriers). The ratio of the number of these effective carriers to the total number of photogenerated carriers is given by

$$\eta=\int_0^{\delta} a e^{-az} dz = 1-e^{-a\delta}, \qquad (1)$$

where a is the absorption coefficient of the substrate. The PID peak height I should correlate with the creation rate of the effective carriers, $F(1-R)\eta$. This relation can be modeled by

$$I=g[F(1-R)\eta]^m = g[F(1-R)(1-e^{-a\delta})]^m . \qquad (2)$$

A nonlinear power dependence $(m \neq 1)$ may occur due to, for example, coupling of the charge movement and the associated change in the band bending at semiconductor surfaces.[15] The parameters g and δ vary with the carrier energy and momentum and therefore photon wavelength and polarization. However, the variations are expected to be limited because of the randomization of hot carriers by scattering.

The dominant mechanism for photodissociation of $Mo(CO)_6$ on the K-free surfaces is identified straightforwardly to be direct adsorbate photoexcitation. The square of the amplitude of the electric field of light wave at Cu and Si surfaces is relatively smooth; the wavelength dependences should be dominated by the $Mo(CO)_6$ absorption spectrum (measured in cyclohexane solution,[16] shown as the dashed lines in Fig. 3). The PID signals [Figs. 3(a) and 3(b)] indeed exhibit the same resonant structure as the absorption spectrum. The sharp peak at 290 nm (4.3 eV) and the shoulder at ~325 nm (3.8 eV) are assigned to metal-to-ligand charge-transfer (MLCT) and ligand-field (LF) transitions, respectively. The photodissociation occurs via a single-photon process, as confirmed by the linear power dependences [Figs. 2(a) and 2(b)].

Ratios of the squares of the amplitudes of the electric fields between s and p waves, on both the vacuum and substrate sides, are calculated from the macroscopic theory[14] using optical parameters given in the literature[17,18] and plotted in Fig. 4 as dotted and solid lines, respectively. (The solid lines are also given by the ratios of $1-R$.) The photoyields due to the direct photoexcitation mechanism on the K-free surfaces [Figs. 4(a) and 4(b)] deviate from the expected correlation with the electric field on the vacuum side. Instead, the PID data lie between the dotted and solid lines, possibly due to microscopic field effects or symmetry breaking of adsorbed $Mo(CO)_6$.[11] In comparison, the data for K-coadsorbed surfaces [Figs. 4(c) and 4(d)] closely follow the solid lines. Thus, the substrate-mediated mechanism is favored since the ratio of the photoyields given by Eq. (2) is $(1-R_s)/(1-R_p)$, assuming polarization-independent g and δ.

The most convincing evidence for the substrate-mediated mechanism comes from the wavelength dependences. On K/Si, the rapid increase in the PID signal near 370 nm [Fig. 3(d)] coincides with the increase in the absorption coefficient of Si (due to the direct-band-gap transition). Assuming that δ and g are independent of wavelength, the PID signal can be fitted by Eq. (2) with $\delta = 12 \pm 2$ nm, as shown by the solid line. The absorption coefficient of Cu is essentially a constant. The photoyield due to the substrate-mediated mechanism is principally determined by $1-R$. The wavelength dependence of $1-R$ of Cu is plotted as the solid line in Fig. 3(c) for $\lambda > 400$ nm, where the PID is solely due to the new channel. An abrupt change in $1-R$ at 580 nm is due to the onset of the d-band transition. The PID signal exhibits a similar change at this wavelength. In contrast, the square of the amplitude of the electric field is relatively smooth and shows no correlation to the photoyield. For $\lambda < 360$ nm, the photoyield is composed of contributions from direct adsorbate photoexcitation and substrate-mediated mechanisms. The lack of significant changes in the electronic transitions of molecular $Mo(CO)_6$ in the presence of K indicates that the cross section for direct adsorbate photoexcitation is not appreciably affected by K.

The electronic levels of physisorbed $Mo(CO)_6$ are approximately fixed to the vacuum level, instead of the Fermi level for chemisorbed species. The highest occupied level of physisorbed $Mo(CO)_6$ is approximately 7 eV below the vacuum level.[19] The LF and MLCT transition energies are ~4-5 eV for $Mo(CO)_6$ in either the gas[16] or the adsorbed phase.[13] So, the empty, antibonding levels of $Mo(CO)_6$ are located ~2-3 eV below the vacuum level. Photogenerated hot electrons can access these $Mo(CO)_6$ levels if they have sufficient energies to meet the energy-conservation requirement and to have appreciable probabilities of tunneling through the barrier between the substrate and $Mo(CO)_6$. The work function of Cu(111) [Si(111)7×7] adsorbed with $Mo(CO)_6$ was measured to be 4.6 ± 0.1 eV [4.7 ± 0.1 eV] and decreased to 2.9 ± 0.1 eV [2.8 ± 0.2 eV] when coadsorbed with K and $Mo(CO)_6$. The large work-function decrease raises the Fermi level towards the vacuum level, allowing photogenerated hot electrons to tunnel through the adsorbate-substrate barrier and attach to the adsorbed $Mo(CO)_6$. The negative ions of $Mo(CO)_6$ formed by electron attachment are known to be extremely unstable towards dissociation.[20]

The K coverage on Cu (Si) for the data reported above is $\Theta_K = 0.15$ ML (0.5 ML) and coincides with the maximum decrease in the work function. In accordance with the above model, the photoyield should depend strongly on the work function which increases rapidly for $\Theta_K < 0.15$ ML (0.5 ML). Using $\Theta_K = 0.05$ ML (0.2 ML) on Cu (Si), it was indeed observed that the PID signal at 436 nm is drastically reduced [only 2% (3%) of the value at $\Theta_K = 0.15$ ML (0.5 ML)], and HREEL and

TD spectra after irradiation exhibit little change compared to those prior to irradiation. Local interaction between K and $Mo(CO)_6$ is inconsistent with the lack of significant changes in the observed electronic transitions, vibrational energies, and thermal-desorption peak temperature of physisorbed $Mo(CO)_6$. Furthermore, it is unlikely that local interaction can give rise to the sharp reduction in the photoyield as the K coverage decreases.

In summary, photodissociation of $Mo(CO)_6$ on the K-free surfaces is identified to proceed predominantly via direct adsorbate photoexcitation. In the presence of coadsorbed K, however, an additional photodissociation channel is opened, which is attributed to dissociative attachment of photogenerated hot electrons to the adsorbed $Mo(CO)_6$. The photoyield is significantly enhanced, and photodissociation occurs even with near-ir irradiation.

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