Laser–Surface-Adsorbate Interactions: Thermal versus Photoelectronic Excitation of $Mo(CO)_6$ on Si(111)

C. E. Bartosch, N. S. Gluck,[a] W. Ho, and Z. Ying

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

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Laser-induced electronic excitation of adsorbed $Mo(CO)_6$ followed by CO desorption is observed to occur on Si(111)(7×7) irradiated with 257-nm (4.8 eV) laser radiation. The process is shown to be completely nonthermal in nature. In contrast, irradiation with 514-nm radiation is found to be identical to resistive heating of the crystal. Adsorption does not open up new excitation mechanisms that allow decomposition to occur in the visible region of the spectrum.

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Understanding the interaction of laser radiation with surface adsorbates is a continuing challenge that has presented formidable difficulties for the experimentalist trying to distinguish between photochemical and thermal interaction mechanisms,[1,2] especially because both effects are often believed to be present.[1] Overcoming this problem offers the potential of selectively driving chemical reactions. To date, most work has relied on calculations to estimate the temperature rise induced by incident radiation rather than direct measurement of the temperature changes. Nonetheless, important work has been accomplished in identifying and understanding laser interactions with surface adsorbates. For example, the absorption of two photons into the N-H stretching mode of weakly adsorbed NH_3 on Cu(100) was shown to lead to nondissociative desorption of NH_3 despite the fact that direct substrate heating effects complicated the analysis.[3] Other groups have identified interactions that are due specifically to direct[4] and indirect[5] substrate heating effects. Direct-band-gap excitation has been postulated to be responsible for XeF_2 etching of Si, but laser heating effects again complicate the interpretation.[6] Recently, laser-induced decomposition of $Mo(CO)_6$ on Si(100) was observed and attributed to photoelectronic effects.[7] Laser decomposition of metallo-organic complexes with subsequent deposition of metallic films has been studied by many groups,[1,2,8] as have surface-catalyzed reactions.[1,2,9,10]

In this Letter, it is shown for the first time that, by direct measurement of the substrate temperature, laser-induced thermal effects can be clearly distinguished from photoelectronic effects. We report an exemplary system of $Mo(CO)_6$ on Si(111)(7×7) where both these mechanisms are separately active under different excitation conditions. High-resolution electron-energy-loss spectroscopy (HREELS) and thermal-desorption spectroscopy (TDS) are used to monitor laser-induced changes in the adsorbed state. In addition, laser-induced desorption (LID) is used to characterize desorption products during laser irradiation. $Mo(CO)_6$ was chosen because in the gas phase the molecule exhibits a high absorption coefficient of $\sim 8000\ \mathrm{cm}^{-1}$ at 257 nm[11] while absorption is completely extinguished in the region of 514 nm. The absorption in the uv is primarily due to electronic excitation involving the metal-ligand charge transfer mechanism and leads to dissociation of the CO ligands from the gas-phase molecule. Adsorption of the molecule on the surface can modify the absorption-decomposition behavior by broadening the absorption band, by introducing new excitation channels, or by offering new deexcitation mechanisms that effectively quench the gas-phase charge-transfer decomposition process. Si(111) was chosen since it is an important semiconductor surface and because CO does not adsorb on defect-free Si(111) at 90 K, considerably simplifying the data analysis.[12]

The experimental apparatus, described in detail elsewhere,[12] consists of a two-level ultrahigh vacuum chamber with a base pressure of 4×10^{-11} Torr. The polished Si(111) wafers were cut into $0.8\times1.25\times0.05$ cm^3 rectangular samples and mounted on a 0.008-cm-thick Ta foil which provides cooling and heating. The temperature was measured with a Chromel-Alumel thermocouple spot welded to a Ta tab that was attached to the back of the Si crystal by the melting of a small piece of Ge over it. All exposures of $Mo(CO)_6$ were performed at ~ 90 K. Monolayer adsorption occurred at ~ 0.7 L [1 L (langmuir) $= 1.0\times10^{-6}$ Torr s]. The results presented in this paper are for exposures in the range from 1.1 to 2.8 L; this variation is not significant since the observed behavior was found to be coverage independent in this exposure range. An Ar^+ laser provided up to 6 W of 514-nm radiation or, when frequency doubled, between 1 and 15 mW of 257-nm radiation. Irradiation was always performed with a Gaussian beam coincident with the crystal center and with a diameter of ~ 0.8 cm at the crystal.

Figure 1 displays four HREEL spectra taken follow-

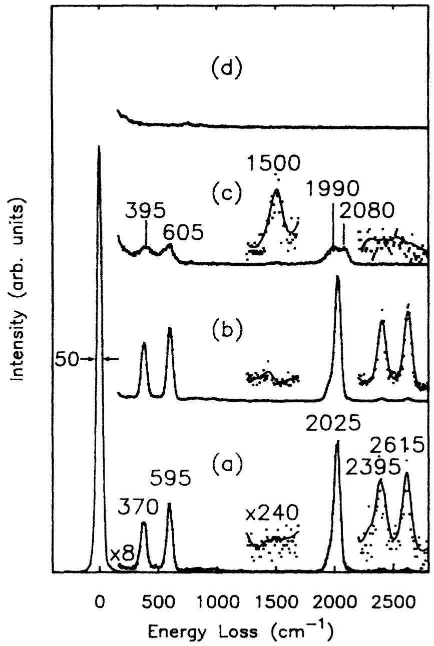

FIG. 1. HREELS of Mo(CO)$_6$ preadsorbed on Si(111) following irradiation under the different conditions explored in the text: (a) no irradiation; (b) low-power (40 mW) 514-nm irradiation for 20 min; (c) 3.8 mW of 257-nm irradiation for 20 min; (d) high-power (2.35 W) 514-nm irradiation for 5 min. Irradiation with low powers of 514-nm radiation has no effect on the spectrum, while all of the CO desorbs with high-power irradiation. The 257-nm radiation partially decomposes the Mo(CO)$_6$.

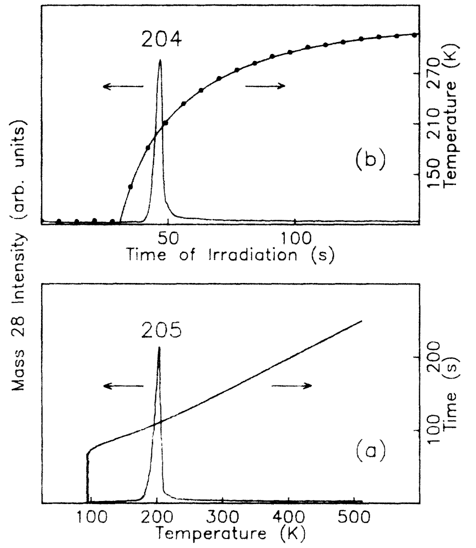

FIG. 2. Mass-28 desorption due to thermal effects. (a) TDS showing desorption vs temperature together with the linear temperature ramp (~2.7 K s^{-1}); (b) LID showing desorption vs time during 1.77 W of 514-nm irradiation together with the laser-induced temperature ramp [for clarity, only one data point in twenty (dots) is shown]. The final temperature reached is 326 K. The laser-induced temperature rise as a function of time is fitted (the solid line through the data points) by the model discussed in the text.

ing different irradiation conditions. Spectrum 1(a) was taken before any laser processing has been performed. A single narrow and intense C-O stretch mode is observed at 2025 cm^{-1} while the Mo-CO stretch and Mo-CO bend modes are observed at 370 and 595 cm^{-1}, respectively.[13] In addition, intense combination bands are observed at 2395 and 2615 cm^{-1}. Spectrum 1(b) was taken following irradiation with 40 mW of 514-nm radiation for 20 min (which produces a temperature rise of 6 K on the Si surface). As is evident in the figure, absolutely no change is observed in peak positions or intensities in HREELS, indicating that low powers of 514-nm radiation do not remove the CO ligands from Mo nor modify the CO bonding character. In contrast, dramatic changes are observed in HREELS following irradiation with uv, as shown in Fig. 1(c) following 3.8 mW of 257-nm radiation for 20 min. The main C-O stretch splits into two peaks centered at 1990 and 2080 cm^{-1} with a much reduced intensity, and a new C-O stretch mode is observed at 1500 cm^{-1}. In addition, the low-frequency region of the spectrum shows broadened, shifted, and reduced intensity peaks at 395 and 605 cm^{-1}. Significant modification of the original carbonyl species has evidently taken place on the surface during the 257-nm irradiation. Finally, Fig. 1(d) shows the results following irradiation with 2.35 W of 514-nm radiation for 5 min (which produces a temperature rise of 288 K). No evidence is seen for any CO groups or even any dissociated C and O on the surface. The spectrum is identical to that obtained following resistive heating of the surface.

Desorption of CO and Mo from the surface was monitored during irradiation. Low powers of 514-nm radiation produced no detectable desorption products, while high powers of 514-nm radiation provided a LID spectrum similar to that observed in TDS. Figure 2(a) shows a TD spectrum and the associated linear temperature ramp (2.7 K s^{-1}) with a CO desorption peak at 205 ± 1 K. Figure 2(b) shows a LID spectrum following irradiation with 1.77 W of 514-nm radiation started ~31 s after the spectrum is initiated. The temperature ramp is about 12 K s^{-1} at the start of the irradiation, but by the desorption peak 15 s later, the ramp is about 3.6 K s^{-1}. The difference in the above heating rates was not found to lead to observable changes in the desorption-peak temperature.[12] Significantly, both the TD and the LID spectra display desorption peaks at ~205 K and full width at half maxima (FWHM) of ~12 K. Mass 96 due to carbonyl desorption is also observed in both the TDS and the high-power 514-nm LID, though no such desorption was observed in the 257-nm or low-power 514-nm irradiation. TDS following the high-power irradiation displays no desorption products related to $Mo(CO)_6$, indicating that no CO remains on the surface.

LID from 2.2-mW, 257-nm irradiation is shown in the upper panel of Fig. 3. Only mass-28 desorption is observed. The desorption is initiated instantly (to within the time response of the mass spectrometer) upon laser irradiation and decays to the background level with further irradiation. The inset in Fig. 3 shows this desorption plotted on a logarithmic-linear scale. As is evident from the figure, a single exponential cannot explain the decay, but rather, a distinct initially fast followed by a slow desorption process is involved.[7,12] The lower panel of Fig. 3 shows TDS following extended (25 min) 3.5-mW, 257-nm irradiation. Dramatic changes are clear in the spectrum. The single desorption peak at 205 K has moved down slightly in temperature, but more significantly, three new peaks are observed at 300, 350, and 435 K. Since Mo is not detected in the LID spectra and CO in a perturbed bonding configuration remains on the surface according to HREELS, it can be concluded that decomposition of $Mo(CO)_6$ has occurred during 257-nm irradiation.

The final sample temperature reached for the clean (or adsorbate-covered) surface as a function of the incident 514-nm power is shown in Fig. 4. At low powers, temperature increases as small as 2 ± 1 K can be measured, as is evident from the inset of Fig. 4. At higher powers, the final temperature is reproducible to ~ ±2 K.

Knowledge of the sample temperature as a function of irradiation is critical to the conclusions drawn here, especially at the front of the crystal where the laser strikes the surface. In view of this, it is necessary to model the expected temperature rise due to irradiation and to estimate the gradient between the front and back surfaces. A similar model has been analyzed elsewhere, but in that calculation the sample was assumed to have zero thickness and perforce identical temperatures on both surfaces.[14] The model developed here assumes that, since the beam diameter is about the same size as the crystal's height, the thermal conduction equation

$$c\,\partial T/\partial t-\kappa\,\Delta T=0 \tag{1}$$

can be reduced to a one-dimensional form

$$c\,\partial T/\partial t-\kappa\,\partial^2 T/\partial z^2=0, \tag{2}$$

where z is the distance along the crystal normal, κ is the thermal conductivity, and c is the specific heat. To make the problem tractable, the conductivity, specific heat, absorptivity, ϵ, and the surface heat transfer function between the Si crystal and Ta foil, h, are assumed to be constant within the experimental temperature range. After appropriate boundary conditions are applied[12] the sample temperature as a function of time, position, and irradiation power, q, is, to a very good approximation, given by

$$T=T_i+\Delta T_c(1-e^{-t/\tau})+\Delta T_b\frac{e^{-t/\tau}-e^{-t/\beta}}{1-\tau/\beta}+\epsilon q z\frac{1-e^{-t/\tau}}{\kappa}, \tag{3}$$

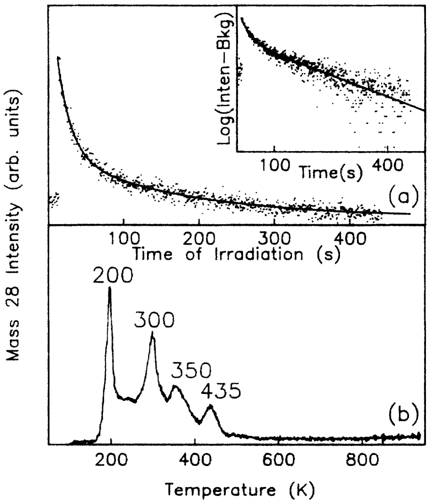

FIG. 3. Mass-28 desorption spectra during and following 257-nm irradiation. (a) LID during 2.2-mW irradiation. Inset: Desorption plotted on a log scale with the background subtracted. The data are fitted by the two first-order exponential decays (solid lines). (b) TDS following extended irradiation with 3.5 mW for 25 min.

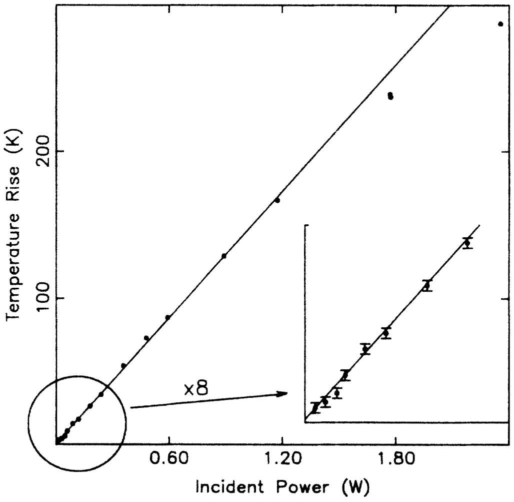

FIG. 4. Net temperature rise vs incident 514-nm radiation power. Inset: An expanded view (×8) of low-power irradiation. Deviation from linearity is observed at high powers and is due to the temperature dependence of the specific heat, absorption coefficient, surface heat transfer coefficient, and thermal conductivity of Si.

where ΔT_c, ΔT_b, τ, and β are fitting parameters. ΔT_c and ΔT_b are the final temperature changes in the crystal and Ta foil, respectively, while τ and β are the characteristic thermal response times of the crystal and Ta foil, respectively. The quality of the fit can be seen by inspecting Fig. 2(b) where the data have been fitted with Eq. (3). Besides being able to model the temperature rise of the sample, Eq. (3) predicts that the largest temperature difference between the front and the back of the crystal is only ~0.05 K for ~2 W cm^{-2} incident radiation.

From the above, it is clear that the temperature increase both measured and expected from 2.2 mW of 257-nm radiation is utterly negligible, despite the dramatic changes observed in the subsequent HREEL and TD spectra. In contrast, an order of magnitude more intense 514-nm irradiation causes no change in either HREELS or TDS. We can conclude that the $\mathrm{Mo(CO)_6}$ decomposition and CO desorption observed by HREELS, TDS, and LID arising from 257-nm irradiation is not due to substrate heating by the laser. The data suggest that the metal-ligand charge-transfer dissociation mechanism observed in the gas phase is also active in the adsorbed state. However, the enhancement in the oxidation of GaAs in aqueous solutions has been attributed to interactions at the interface with the hot carriers created within ~50 nm of the surface by the 257-nm radiation.[15] Although this mechanism could also be active at the gas-solid interface, detailed calculations of the energy levels and carrier dynamics, and further experiments on other adsorbates and surfaces, are needed to assess its importance.

Irradiation with high incident powers of 514-nm radiation desorbs all resident $\mathrm{Mo(CO)_6}$. Since the desorption temperature remains the same whether the desorption is induced by resistive heating or 514-nm radiation, any band bending due to photogenerated electron-hole pairs is not affecting the binding energy.[6] Likewise, it is evident that electron-hole pair-recombination events are not coupling to the adsorbates, ruling out a potential excitation channel opened by adsorption. Since we are well below the multiphoton absorption region, it is clear that irradiation in the high-power regime must induce surface heating alone.

In summary, the surface temperature of Si has been directly measured during irradiation, allowing an unambiguous distinction to be made between thermal and photoelectronic excitation of $\mathrm{Mo(CO)_6}$ on Si(111)(7×7). The identity between the front surface temperature and that measured at the back of the crystal has been verified by a model calculation and by comparison of TDS and LID results where desorption occurs at the same measured temperature. At powers insufficient to induce a measurable temperature rise, 257-nm irradiation not only induces CO desorption but also induces distinct changes in the subsequent HREEL and TD spectra indicative of $\mathrm{Mo(CO)_6}$ decomposition. Because an order of magnitude higher power density of 514-nm radiation leads to no desorption or alterations in the HREEL or TD spectra, direct electronic interaction of the 257-nm radiation with the adsorbed species is evident, and is very likely the same charge-transfer mechanism which is active in the gas phase. New excitation mechanisms due to adsorption of $\mathrm{Mo(CO)_6}$ on Si(111) need not be invoked, nor are fast deexcitation channels that could quench the gas-phase decomposition reaction observed.

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[a] Present address: School of Applied and Engineering Physics, Cornell University, Ithaca, NY 14853.

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