Femtosecond Time-Resolved Surface Reaction: Desorption of Co from Cu(111) in < 325 fsec

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The laser-induced desorption of CO molecules from a Cu(111) surface is time resolved with 100-fsec resolution. We find the desorption reaction is completed in ≤ 325 fsec after the 100-fsec, 2-eV photon energy pump pulse. The only mechanism consistent with this abrupt, efficient ($\sigma \sim 10^{-18}$ cm^2) desorption is a novel one: The transient hot substrate electrons ($T_{electron,max} \sim 3600$ K, while $T_{lattice,max} \sim 160$ K) drive *multiple* electronic excitation-deexcitation cycles of the CO-Cu complex within the vibrational relaxation time. Such cycles leave the molecules vibrationally excited in the ground state potential which enhances the desorption on subsequent electronic excitations.

A most challenging goal in the field of surface physics has been to develop techniques by which dynamics at surfaces can be resolved on the time scale of energy transfer between the various degrees of freedom of the adsorbate-substrate complex, i.e., subpicosecond. Such techniques would provide a means for directly observing the microscopic mechanisms which make up dynamic processes. So far there has been notable success in ultrafast time-resolved studies of excited-state electronic [1] and vibrational [2] relaxation at surfaces and in the study of ultrafast surface phase transitions [3]. In this Letter, we report the first subpicosecond measurement of the time evolution of a surface chemical *reaction*, i.e., the making and breaking of chemical bonds on surfaces. Specifically, we report that CO molecules desorb from a Cu(111) surface within 325 fsec after irradiation with 100-fsec, 2-eV photon energy laser pulses.

In previous studies of laser-induced desorption [4,5], the properties of *desorbed* molecules were measured. While informative, such studies do not allow direct measurement of the time that the molecules actually desorb from the surface. Here, we use second-harmonic generation (SHG) as a time-resolved probe of the coverage of *adsorbed* molecules. We are thus able to measure the time of desorption with a resolution limited only by the accompanying SH response due to substrate heating. The observation of a surprisingly short desorption time allows us to identify the desorption mechanism. We find that the 100-fsec pulses induce desorption by a mechanism distinct from all conventional ones.

The experiments were performed on the well-characterized system CO/Cu(111) [6,7] held in UHV at saturation coverage [$\theta_{sat} \sim 0.52$ monolayer (ML) [6]] at a temperature of 95 K. At saturation coverage, the LEED pattern is (1.4×1.4) and ir studies show that the CO molecules occupy both bridge and atop sites [6(a)]. The 100-fsec laser pulses were generated by amplifying the output of a colliding-pulse mode-locked (CPM) dye laser operating at ~620 nm. The amplified output was split into a strong pump and a weak probe beam which were overlapped on the Cu surface. Both beams were *p* polarized and made nearly "top-hat" in spatial profile.

Figure 1 (left-hand side) shows the dependence of the SH probe signal on CO exposure (no pump beam). The coverages indicated are those assigned by Raval *et al.* [6(a)]. On the right-hand side of this figure, we show the change in SH signal due to desorption from the CO-saturated surface by a *single* 100-fsec laser shot of 4.5 mJ/cm^2 absorbed fluence. This observed change is due only to desorption of CO molecules. First, there is no permanent change in the substrate: There is no change in the SH signal level when the experiment is repeated on a clean surface, nor could we observe any difference in the LEED pattern, Auger spectra, absolute SH signal level, or SH dependence on CO exposure for parts of the surface exposed or never exposed to the pump pulse. Second, we rule out dissociation because there is no change in the SH signal level for a CO-saturated surface after many ($> 10^3$) laser-desorb–redose–probe cycles and thus no accumulation of fragments on the surface (as observed in [5(c)]). The mass spectrometer also shows no sign of dissociation. Finally plasma or charged-particle effects are negligible for our pump intensities. We measured the electron emission to be $< 10^{-5}$ that of the desorbed CO molecules, and the positive ion emission to be immeasurably small ($< 10^{-8}$).

Figure 2 shows the result of the pump-probe experiment at the same pump and probe laser intensities as in Fig. 1. We also show the pump-probe autocorrelation generated by sum frequency (SFG) *on* the Cu surface.
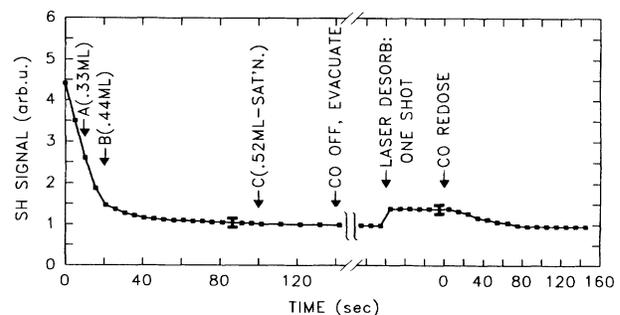

FIG. 1. Left-hand side: SH signal vs exposure ($P_{CO} \sim 5 \times 10^{-8}$ torr). A,B,C refer to LEED patterns observed (see [6(a)]). Right-hand side: Desorption due to a single laser shot of 4.5 mJ/cm^2, and then redosed as above.
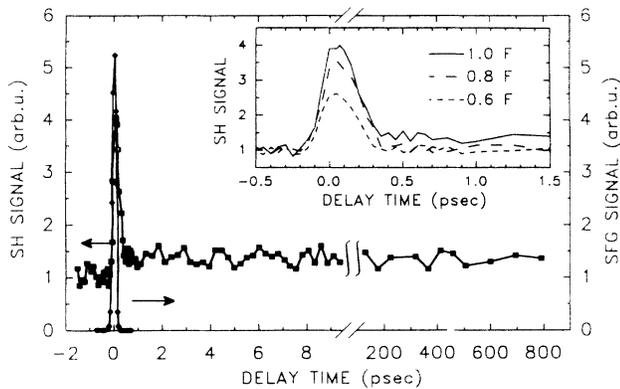
FIG. 2. SH probe signal vs delay time after the desorption-inducing pump beam. Fluence (F) of pump $=4.5$ mJ/cm^2. Intensity autocorrelation also shown (SFG). Inset: Same data (solid line) on expanded time scale, with two other fluences.
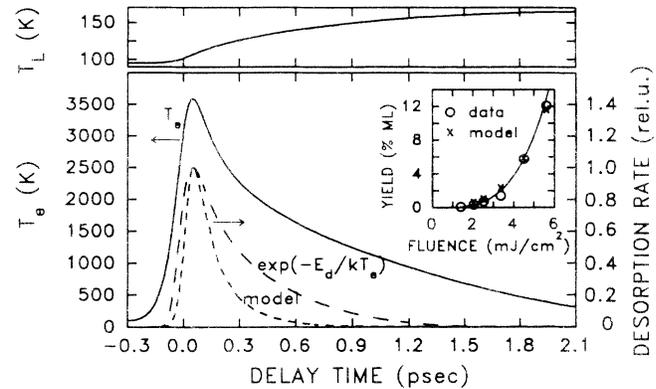

FIG. 3. Solid line: Electron and lattice temperatures vs delay time after 4.5 mJ/cm^2 absorbed pump pulse (calculated). Long dashes: Desorption rate for case of $\exp(-E_d/kT_e)$, where $E_d = 0.4$ eV [6]. Short dashes: Desorption rate calculated using model (multiexcitation of 2π) described in text. Inset: Desorption yield vs absorbed laser fluence. Here, the calculated yield is multiplied by 4 to normalize to the measured yield at 4.5 mJ/cm^2.

The inset shows the same data on an expanded scale together with results using two lower fluences, $0.6F$ and $0.8F$. The spike in the SH signal near zero time delay is due to a real SH response which is enhanced by ~ 2 at zero delay because of the coherent artifact. The probe SH signal then falls to a constant baseline by ~ 350 fsec which is (a) persistent and (b) at the same level as that shown in Fig. 1 due to desorption of CO molecules with a *single* laser shot. All three baseline shifts are consistent with the SH versus coverage data of Fig. 1 and the yield versus fluence data of Fig. 3.

In general, the SH response will be due to both the desorption of molecules (change in coverage) and electronic excitation of the surface. As soon as the electronic excitation response is over, a constant baseline means the desorption event is also over. We now reason from the three fluence curves that the electronic excitation response is over by 350 fsec. Our argument is twofold. First, because the baseline shift is small in the $0.6F$ and $0.8F$ curves, we may identify the electronic excitation response in those data as the spike features which are over in < 350 fsec. The decay of the electronic excitation response in the $1.0F$ curve should be the same. This is because the excitation decays via thermalization to a Fermi-Dirac distribution and diffusion into the substrate at rates which do not depend on fluence over this small range. The SH data support this. Fitting the three data curves by $SH(t) \propto |\chi_0 + \Delta\chi(t)|^2$, where χ_0 and $\Delta\chi(t)$ are the initial and transient SH susceptibilities, we find that the rapidly varying part of $\Delta\chi(t)$ for the $1.0F$ curve is identical to the normalized $\Delta\chi(t)$ for the $0.8F$ curve. The decay of $\Delta\chi(t)$ for the $0.6F$ curve is only slightly faster. By this fit procedure, we find that the excitation spike in the $1.0F$ data is also over in 350 fsec. Second, it is extremely unlikely that the constant SH baseline shift for delay times > 350 fsec is due to anything other than the desorption being over in < 350 fsec. Any further SH response to electronic excitation would have to (a) have

the magnitude and time dependence to exactly compensate for the desorbing molecules, and (b) do so for all fluences in the range $(0.6-1.0)F$. We conclude then that the SH response to electronic excitation is over in 350 fsec for all three fluence curves in Fig. 2; the constant shifted baseline after that point means that the desorption is also completed before then. Deconvolution of the data with the 100-fsec laser pulse duration and a conservative estimate of our signal to noise gives that $> 90\%$ of the desorption is complete in < 325 fsec.

Figure 3 (inset) shows that the desorption yield (measured with a mass spectrometer) increases nonlinearly with the intensity and can be fitted by the power law $\sim I^{3.7}$ (solid line). For the case of 4.5 mJ/cm^2 absorbed energy, the yield is ~ 0.05 ML, giving a quantum efficiency of $\sim 10^{-3}$/absorbed photon (cross section $\sim 10^{-18}$ cm^2). This cross section is much higher (by $\sim 10^3$) than that observed in previous molecule/metal photochemistry studies done using conventional visible sources [4(b),5,8]. It is important to note that the superlinear yield in our experiment cannot be explained by coverage-dependent desorption kinetic effects. The yield dependence could only be explained in this way if the desorption got easier with decreasing coverage. If anything, we find the opposite: CO gets slightly harder to desorb as the coverage decreases to $\frac{1}{3}$ ML ($\sqrt{3}\times\sqrt{3}R\,30°$ LEED pattern), desorbing at approximately a constant fraction of θ. After $\frac{1}{3}$ ML, it gets much harder to desorb.

To understand these results, note that subpicosecond laser excitation can induce a transient electron temperature which is much higher than that of the lattice [9]. The coupled diffusion equations which give $T_e(t)$ and $T_{lattice}(t)$ have been presented previously [9]. Our own

numerical solution (Fig. 3) for the conditions of our experiment [10] gives $T_{e,max} \sim 3600$ K occurring < 100 fsec after zero time delay, while $T_{lattice,max} \sim 160$ K, occurring ~ 2 ps after zero delay. This treatment ignores the finite time for the electron and phonon distributions each to thermalize at $T_{e,lattice}$. However, by the time $T_{e,max}$ is reached we do not expect the deviation from a Fermi-Dirac (FD) distribution to be significant for our purposes [11].

We now identify the desorption mechanism. It is found that only one is consistent with both (a) the ultrafast turn-on and turn-off times observed and (b) the high and nonlinear yield. First, we rule out all mechanisms in which the turn-on or turn-off times would be too slow. This eliminates all thermal and thermally assisted (caused by $T_{lattice}$) mechanisms since the desorption is completed even before the lattice heats up (see Fig. 3). We also eliminate all mechanisms of desorption that are driven by local vibrational modes (surface phonons and/or the CO-metal vibration) *thermally* equilibrated with the hot electrons because the desorption rate would go as $\exp(-E_d/kT_e)$. An important example is dipole coupling between the electrons and vibrational modes. Even if dipole coupling were able to instantaneously give $T_{vib} = T_e$, the desorption rate would be too slow (see Fig. 3, long dashes) [12]. The finite equilibration time between the hot electrons and vibrations would result in an even slower turn-off time [13]. Finally, we eliminate mechanisms driven by a superthermal substrate phonon distribution because such a distribution is unlikely in Cu which is free-electron-like within 1 eV of E_F.

Only one class of desorption mechanism now remains: electronic excitation. Previous work indicates that electronic desorption could occur in this and related systems through a variety of paths, via Menzel-Gomer-Redhead-type (MGR) schemes [14,15]. Of these electronic mechanisms, we can immediately exclude desorption due to the direct, intramolecular (four-photon) 5σ to 2π transition: Even if the efficiency for desorption from this excited state were ~ 1, the four-photon optical absorption would have to be an impossibly large $\sim 1\%$ to satisfy the high yield. Using similar cross-section arguments, we exclude all other mechanisms involving 5σ (located ~ 7 eV below E_F [7,16]): both substrate-mediated multiphoton (nascent) and thermalized hot hole excitation. Finally, we rule out as dominant the direct one-photon transition from the metallic states near E_F to the adsorbate 2π states (located 1–1.5 eV above E_F [16,17])—i.e., the *nascent* hot electrons exciting 2π: This mechanism would give a linear dependence of yield on absorbed laser fluence (as seen in [5(b)]).

The only mechanism consistent with both the ultrafast desorption time and the superlinear dependence of yield on absorbed fluence is that the hot *substrate* electrons, thermalized at $T_e \sim 3600$ K, electronically excite the 2π level of the adsorbed CO molecule so that it desorbs. The 2π excitation rate resulting from this CO-Cu coupling is

extraordinarily high. This is because the 2π level is so strongly coupled to the substrate electrons (2π lifetime ~ 1-10 fsec [18]) that its occupation is given by the substrate electron distribution function $f[E, T_e(t)]$ (taken here to be FD). The rate of excitation which leads to desorption is then given by

$$G(t) = \tau_{exc}^{-1} \int_{E_{thr}}^{\infty} f[E, T_e(t)] DOS(E) dE$$
$$+ \alpha \int_{E_{thr}}^{2} I(t) DOS(E) dE,$$

where τ_{exc} is the lifetime in the 2π excited state, E_{thr} is the threshold electron energy which induces desorption, $\alpha I(t)$ describes the energy absorbed by the laser pulse, and $DOS(E)$ is the 2π density of states. If we take $DOS(E)$ to be a Gaussian of width 1.7 eV centered at 1.0 eV [16,17], $\tau_{exc} = 3$ fsec, $E_{thr} = 0.5$ eV, and $T_e(t)$ to be that shown in Fig. 3, the time-integrated $G(t)$ for the thermalized electrons (first term only) is ~ 2.5 excitations per molecule (for $E_{thr} = 0$, it is 10 excitations per molecule). This is much larger than the ~ 0.1 excitation per molecule from the nascent electrons (second term).

For this and related systems, the substrate-to-2π electronic excitation transfers charge from the metal to the molecule. The induced image charge accelerates the molecule toward the surface [14,15,19]. Deexcitation from the 2π state then leaves the molecule vibrationally excited in the ground-state potential; desorption occurs if the vibrational energy exceeds the binding energy. Because the 2π excitation rate is so high in our experimental case, a novel mechanism for desorption becomes possible. Multiple excitation-deexcitation cycles within a time short compared to the vibrational relaxation time on the ground-state potential can pump the CO molecule to higher vibrational energies than possible with single excitation—this leads to increased desorption probability.

There are thus two effects which can together explain the high and nonlinear yield: (a) the nonlinear dependence of $G(t)$ (2π excitation rate leading to desorption) on absorbed laser fluence via the electron temperature, and (b) the nonlinear dependence of the desorption rate on $G(t)$ via multiple excitations. It is important to note that (a) alone does not provide enough nonlinearity unless an unrealistic value of $\tau_{exc} \leq 0.2$ fsec is chosen [19]. Thus an additional nonlinearity such as that provided by multiple excitations must be invoked to explain our experimental results.

To examine the relative importance of multiple excitations and whether effects (a) and (b) together can account for our experimental results, we developed a simple mathematical model. This model relies on an excited-state potential which provides acceleration to the CO species. For one-half of the CO-metal vibrational period, some average vibrational energy ΔE is gained (+) for each excitation to 2π, corresponding to an average change in vibrational energy band of $\Delta n = 1$; for the other half of this cycle, this energy is lost ($-$). After each excitation, desorption occurs with probability $\exp[-\tau_{des}/n\tau_{exc}]$,

where τ_{des} is the time required for the CO species to evolve into the configuration of no return in the excited state. The model is embodied in two equations (+, for acceleration, and −, for deceleration): $(df_n/dt)^{\pm}$ $=\{f_{n\pm1}(1-\exp[-\tau_{des}/n\tau_{exc}])-f_n\}G(t)$, where f_n is the fraction of molecules populating the vibrational energy band n ($=1$ to ∞). To solve this model we average over all initial CO positions. We find that for reasonable parameters ($\tau_{exc}=3$ fsec, $\tau_{des}=12$ fsec, and $E_{thr}=0.8$ eV) we can reproduce all of the experimental results quite well (Fig. 3) [20]. In particular, we find that ∼70% of the yield comes from multiple excitations (≥ 2). A more detailed discussion of this model will be given in a subsequent publication.

In summary, we observe that CO molecules desorb from a Cu(111) surface in ≤ 325 fsec after irradiation by a 100-fsec, 2-eV photon energy laser pulse. We find the desorption yield is high and has a superlinear dependence on absorbed fluence. This work establishes that a novel desorption mechanism operates here under 100-fsec optical laser irradiation: A hot *electronic* temperature is induced in both the substrate and the adsorbate. The resulting adsorbate electronic excitation rate is so high (>20 times the direct photoexcitation rate) that multiple excitation-deexcitation cycles can occur within the vibrational relaxation time. This vibrationally pumps the molecules up the ground-state potential, enhancing the desorption on subsequent electronic excitations.

Finally, we remark that this 100-fsec time-resolved technique can immediately be applied to studies of other surface dynamic phenomena: e.g., even reactions not involving desorbed species, as well as transient surface chemical intermediates such as precursors.

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[10] g (electron-phonon coupling) $=7\times10^{10}$ W/cm^{3}K [[9(b)]; P. B. Allen, Phys. Rev. Lett. **59**, 1460 (1987)]; $C_e=\gamma T_e$ ($\gamma=9.46\times10^{-5}$ J/cm^3 K^2); $C_l(T)$ given by A. P. Miller *et al.*, Can. J. Phys. **49**, 704 (1971); κ (thermal conductivity) $=3.85T_e/(T_l+1.37\times10^{-5}T_e^2)$ W cm^2/K. This form for κ follows [9(c)] where the T dependence of electron-electron scattering is calculated using the free electron model and scaled with the data of J. J. Quinn [Appl. Phys. Lett. **2**, 167 (1963)].

[11] Small deviation from FD distribution for low-energy electrons (0.1–0.2 eV) has been reported in gold for delay times ∼500 fsec by W. S. Fann *et al.* (to be published). In our experiment, the electrons that couple to CO (≥ 1 eV) reach an FD distribution in <80 fsec and their decay by diffusion into the bulk is adequately modeled by the approach used here.

[12] We use a constant prefactor here because both E_d [6] and our measured desorption rate coefficient (from yield versus coverage data) from 100-fsec laser pulses are independent of coverage over the small range of relevance, $(0.95-1.0)\theta_{sat}$.

[13] We can assume the CO-Cu stretch vibrational lifetime at 100 K to be similar to that for CO-Pt(111), i.e., $\gtrsim 10$ psec [$\Delta\bar{\nu}=0.8$ cm^{-1}; B. N. J. Persson and R. Ryberg, Phys. Rev. B **40**, 10273 (1989)]. Since dipole coupling scales as the optical density of states at the stretch frequency, at $T_e=3600$ K the coupling increases by 10 and the equilibration time is >1 psec.

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