Hot Carrier Excitation of Adlayers: Time-Resolved Measurement of Adsorbate-Lattice Coupling

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Picosecond time-resolved infrared absorption measurements of CO/Cu(100) following visible and ultraviolet laser pumping allow a determination of the time scales for photoexcited carriers and lattice phonons to couple to the CO frustrated translation vibrational mode.

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Since low frequency vibrational modes of adsorbates are the precursors to motion about and away from a surface, energy transfer through these modes plays important roles in a wide range of interface processes. For example, calculations of surface diffusion rely upon knowledge of the frictional damping rates of frustrated translations [1]. Reactions between molecules on neighboring sites rely on activation of these modes to bring the molecules together. Recently, the field of femtosecond surface photochemistry has opened up a realm of novel interactions of molecules with nonequilibrium substrate degrees of freedom. Ultimately, an understanding of these processes requires knowledge of the various pathways by which the low frequency modes can couple to the substrate degrees of freedom [2-5]. However, the low cross sections for optical absorption and the lack of available time-resolved spectroscopies at these frequencies have prevented the direct measurement of the lifetimes of these modes.

By observing the vibrational response of an adsorbate during ultrashort laser heating of a substrate, the time scales and mechanisms for surface-molecule energy transfer can be revealed. In this Letter, time-resolved measurements of the transient response of CO/Cu(100) to picosecond laser excitation are presented. Unlike previous measurements of substrate-adsorbate coupling strengths [6], these results unambiguously establish the contribution of transiently heated substrate electrons and phonons in activating the low frequency adsorbate vibrational modes and allow the coupling times of the frustrated translational mode to hot carriers and phonons to each be determined.

The 0.5 monolayer (ML) (1 ML$=7.67\times10^{14}$ cm^{-2}) $(\sqrt{2}\times\sqrt{2})R45°$ overlayer of CO on Cu(100) at 100 K has been well characterized in terms of both adsorbate vibrational modes and low lying unoccupied electronic states. The electronic levels of the system have been characterized using inverse photoemission, indicating two unoccupied levels centered at 2.6 and 3.6 eV above the Fermi level, related to the CO 5σ and $2\pi^*$ levels [7,8]. Infrared reflection-absorption spectroscopy (IRAS) [9,10] and helium atom scattering [11] have identified the four fundamental vibrational modes: the CO stretch at $\nu_1=2086$ cm^{-1}, the Cu-CO stretch at $\nu_2=345$ cm^{-1}, the frustrated rotation at $\nu_3=285$ cm^{-1}, and the frustrated translation at $\nu_4=32$ cm^{-1}. We have made independent steady state IRAS measurements [12] on the same crystal used for the time-resolved experiments, determining the temperature dependence of the CO stretch mode $\nu_1=2086-0.031[T(\mathrm{K})-100]$ cm^{-1} and width $\delta\nu_1=3.9+0.005[T(\mathrm{K})-100]$ cm^{-1}. This behavior is readily accounted for by dephasing of the CO stretch by anharmonic coupling to the frustrated translation mode [12,13]. We will show that this same mode couples to transiently heated substrate electrons on the picosecond time scale.

The apparatus for the time-resolved experiments is described elsewhere [6]. In brief, probe light centered near 2086 cm^{-1} is focused with a Gaussian beam radius $w=120$ μm onto a Cu(100) crystal at an 88° angle of incidence. The probe light is polarized at roughly 45° to the plane of incidence so that it contains both s and p components. Upon reflecting from the sample, the probe light is dispersed in a polarization-preserving monochromator with 1 cm^{-1} resolution before striking two InSb detectors, one of which senses only p, and the other only s polarization. For transient response measurements, a p-polarized visible (579 nm, 230 μJ) or ultraviolet (289 nm, 17 μJ, generated by doubling the visible light in KDP) pump is focused onto the sample at an 87° angle of incidence. The transient spectral differences are reported as changes in optical density [6,14]. The relative arrival times t_d of the pump and probe at the sample are controlled with an optical delay stage. Cross correlations by sum and difference frequency generation of the pump and probe in a thin LiIO$_3$ crystal are consistent with sech^2 pulse durations of 1.2, 1.2, and 0.8 ps for the infrared, visible, and ultraviolet light, respectively. No cumulative spectral changes were observed that could be attributed to laser-induced changes in CO coverage using either pump wavelength.

Figure 1 shows a transient difference spectrum near $t_d=0$ ps for the visible pumping conditions. Aside from differences in magnitude, the data look identical for ultraviolet pumping. This derivativelike signal is characterized by a transient reduction in the reflectivity near 2085 cm^{-1} with a simultaneous increase in reflectivity near 2087 cm^{-1}, resulting from a shift of the Lorentzian CO

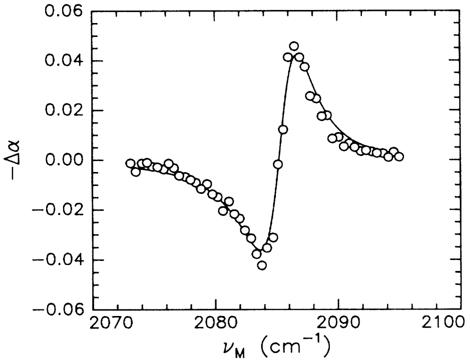

FIG. 1. Transient difference spectrum of CO/Cu(100) at $t_d=0$ and $T=100$ K induced by 579 nm pumping. The curve drawn through the data represents calculated spectra as described in the text.

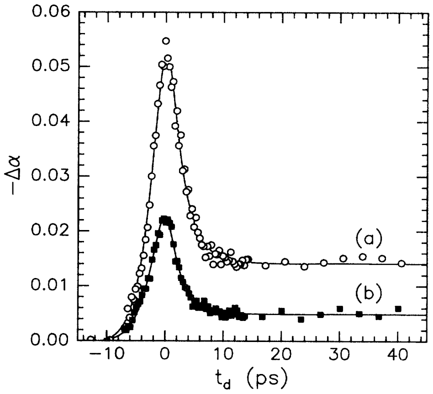

FIG. 2. Transient difference at 2087 cm^{-1} as a function of pump-probe delay time t_d after (a) 579 nm pumping and (b) 289 nm pumping. The curves drawn through the data represent best fits to the model described in the text.

stretch absorption feature to lower frequencies. Figure 2 shows the time dependence of the transient response to visible and ultraviolet pumping, where the transient difference is sampled with the spectrometer set at 2087 cm^{-1}, i.e., 1 cm^{-1} higher in energy than the 100 K CO stretch feature. For the 579 nm (289 nm) pump measurements, a distinct peak is observed near $t_d=0$, which decays with a characteristic time constant $\tau=2.6\pm0.4$ ps (2.3 ± 0.3 ps) to an intermediate level, about 0.26 ±0.02 (0.22 ± 0.04) that of the peak signal. The intermediate signal then decays on a time scale of ≈ 200 ps. The uv signal is smaller than the visible because the amount of uv light initially generated and subsequently absorbed by CO/Cu(100) was less.

The substrate response can be described as follows. Upon absorption of light, nascent carriers with $E\leq h\nu$ will be generated. The nascent electron distribution can be estimated from the band structure of copper. Following the technique described by Smith [15], a joint density of states calculation gives electron energies between 0 and 0.55 eV above the Fermi level for 579 nm light and energies between 0 and 2.7 eV and between 3.6 and 4.3 eV above the Fermi level for 289 nm light. This distribution shows primarily excitation of electrons from the top of the *d* band. Similarly, holes will be generated at the corresponding energy below the Fermi level. These carriers will inelastically scatter from other carriers or from the lattice on a time scale of 10–100 fs [16], resulting in a Fermi-Dirac distribution with a temperature T_e, differing from the lattice temperature $T_{\rm lat}$. The Fermi-Dirac electrons couple to the lattice phonons on a ps time scale decreasing T_e and increasing $T_{\rm lat}$.

A standard two-temperature heat diffusion model, separating the electronic and lattice degrees of freedom [17], was used to calculate T_e and $T_{\rm lat}$ as functions of time and distance into the surface for the conditions of this experiment. Figure 3 shows the calculated T_e and $T_{\rm lat}$ evaluated at the surface as a function of time for the visible pump [18]; the calculated temperature jumps were $\Delta T_e^{\rm max}=225$ K and $\Delta T_{\rm lat}^{\rm max}=7.5$ K, respectively. On approximately a 200 ps time scale, the coupled surface T_e and $T_{\rm lat}$ decay by heat transfer into the bulk.

The data in Figs. 1 and 2 can best be accounted for by coupling of the frustrated translation dephasing mode to both T_e and $T_{\rm lat}$. The transient frequency shift of the CO stretch absorption, which causes the IR transients, is attributed to the change in ν_4 population, i.e., to the temperature of that mode: $\langle n_4\rangle=[\exp(h\nu_4/kT_{\rm ads})-1]^{-1}$ $\approx kT_{\rm ads}/h\nu_4$. Using the calculated substrate response in Fig. 3, the interaction of the frustrated translation with the electron and lattice baths can be modeled using a third temperature. The dephasing mode temperature $T_{\rm ads}$ is assumed here to couple with characteristic coupling times $\tau_{\rm lat}$ and τ_e to both the electron and lattice heat baths according to

$$dT_{\rm ads}/dt=(T_e-T_{\rm ads})/\tau_e+(T_{\rm lat}-T_{\rm ads})/\tau_{\rm lat}\,.$$

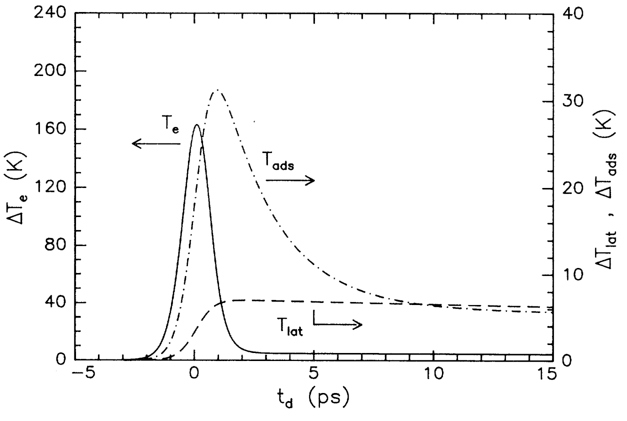

FIG. 3. Calculated electronic, lattice, and frustrated translation temperature jumps (ΔT_e, $\Delta T_{\rm lat}$, and $\Delta T_{\rm ads}$) as functions of time for the conditions of this experiment with $\tau_e=5.1$ ps and $\tau_{\rm lat}=4.2$ ps.

To model the data shown in Figs. 1 and 2, the spectral response of the adlayer to picosecond pump and probe pulses has been calculated, accounting for the finite coherence time of the adlayer using a density matrix method which has been presented elsewhere [14]. The density matrix approach accounts for the rise of the response (Fig. 2) starting at $t_d \approx -6$ ps. This $t_d < 0$ response, rather than violating causality, is a perturbed free induction decay; the rise time indicates T_2 for the sample and not the laser pulse duration. In this model, the frequency and width are considered to be linear functions of T_{ads} determined by the aforementioned $\nu_1(T)$ and $\delta\nu_1(T)$. In Figs. 1 and 2, the curves drawn through the data represent nonlinear least squares best fits to this model. Figure 3 shows T_{ads} as a function of time. As a result of uncertainties in the pump fluence actually absorbed by the sample (laser spot size at the crystal, angle of incidence, and window transmission affect this), the fluence was treated as a free parameter and was chosen to fit the long time data. The visible pump data are best modeled with $\tau_e = 5.1 \pm 0.4$ ps and $\tau_{\mathrm{lat}} = 4.2 \pm 0.7$ ps, while the ultraviolet pump data are best modeled with $\tau_e = 3.9 \pm 0.4$ ps and $\tau_{\mathrm{lat}} = 3.9 \pm 0.8$ ps. With the present signal-to-noise ratio, the normalized temporal evolution observed for 4.28 eV excitation is indistinguishable from that observed for 2.14 eV.

The uncertainties in the values reported above are 67% confidence limits determined by evaluating χ^2 over the parameter space near the minimum. The errors in these coupling times, however, are dominated by the uncertainties in the parameters used to model the substrate response [18]. The measured adlayer decay is the sum of the two rate constants $1/\tau_e + 1/\tau_{\mathrm{lat}}$. The best fit value for τ_e depends empirically on the choice of the electron-phonon coupling constant g according to $\tau_e(\mathrm{ps}) = 4.25/g(10^{17}\ \mathrm{W\,m^{-3}K^{-1}}) + 0.85$. Although we used the estimate $g = 1.0 \times 10^{17}\ \mathrm{W\,m^{-3}K^{-1}}$ from recent fs laser pump/probe experiments [18], there are other estimates in the range 0.47–$1.0 \times 10^{17}\ \mathrm{W\,m^{-3}K^{-1}}$, and fitting the visible pump data to T_e calculated from the lesser estimate would give $\tau_e = 9.9$ ps and $\tau_{\mathrm{lat}} = 3.1$ ps.

We have shown that direct excitation of the CO stretch mode causes a population dependent shift in the CO($v = 0 \rightarrow 1$) transition to lower frequencies [12,14]. However, the magnitude of the $t_d = 0$ signal rules out ν_1 population as causing the observed transient. The observed signal would require roughly 4% of the CO population to have been excited to the $v = 1$ band, corresponding to a vibrational temperature of ≈ 1070 K. The value of $T_e^{\max}$ in Fig. 3 would give a CO($v = 1$) population $\approx 1 \times 10^{-4}$. Also, since the electron-hole pair coupling for the CO stretch is not instantaneous, but has been previously measured [19] to be about 2 ps, the CO stretch vibrational population could only reach $0.4 T_e^{\max}$ before T_e decreased to T_{lat}.

The 2.5 ps time scale of the signal decay near $t_d = 0$ rules out direct dephasing of the molecule by the hot electrons, since the decay of the signal would have to occur as quickly as T_e decays, which is essentially the pump pulse duration. In addition, the time scale of this decay eliminates field induced changes [20] in frequency of the CO($v = 0 \rightarrow 1$) transition as this is also expected to decay as the pump pulse envelope.

The lack of any substantial difference in response between the two pump wavelengths, despite the strikingly different nascent electron distributions, argues strongly against any mechanism involving ballistic electrons causing the measured transient. In particular, excitation of the unoccupied CO $2\pi^*$ electronic levels in these experiments can be ruled out as a significant source of the transient signal.

Transient population of the low frequency modes ν_2 or ν_3 could conceivably contribute to dephasing of the CO stretch mode. CO desorbs from Cu(100) at $T = 180$ K, so steady state IRAS experiments can only be done at T sufficiently low that ν_2 and ν_3 are not significantly populated. Hence, the strength of the anharmonic couplings between ν_1 and ν_2 or ν_3 is unknown. For $t_d \gtrsim 15$ ps, the entire transient can be accounted for by population in ν_4, since the well established ν_4 induced shift reproduces the observed signal, and since ΔT_{lat} and ΔT_e are so small that ν_2 and ν_3 are not populated. Therefore, it seems unreasonable to ascribe the transient near $t_d \approx 0$ to population in ν_2 or ν_3 rather than to the established coupling to ν_4.

There has been substantial theoretical controversy about whether low frequency adsorbate vibrational modes exchange energy faster with lattice phonons or with electron-hole pairs. A frequently invoked rule of thumb is that relaxation is dominated by coupling to phonons if the frequency of the surface mode, ν_s, is less than twice the Debye frequency, ν_D, so that only one or two phonons need be created in the relaxation of ν_s. For $\nu_s > 2\nu_D$, the higher order of the multiphonon process would make phonon damping less efficient than electron-hole pair formation, which is thought to increase with ν_s due to an increased density of states. A contrary argument is that relaxation of low frequency modes by phonon emission is unimportant, compared to electron-hole pair damping. The coupling time of the frustrated translational mode of CO/Cu(100) to phonons is estimated from the elastic continuum model of Persson and Ryberg [21] to be $\tau_{\mathrm{lat}} = 8\pi(c_T/\nu_4)^3/3m\nu_4 = 15$ ps, where m is the CO mass, ρ is the density of copper, and c_T is the transverse sound velocity.

Persson [22] has used CO induced changes in thin copper film resistivity and Cu(100) infrared reflectivity to estimate the frictional coupling between the frustrated translation and the substrate electrons to be in the range of 36–56 ps, in poor agreement with our measured τ_e. Head-Gordon and Tully have carried out a series of *ab initio* calculations for the vibrational lifetimes of CO adsorbed onto copper clusters [23]. Their calculations include the effects of coupling to both phonons and electron hole pairs simultaneously. They calculated the relaxation time of ν_4 to be 14 ps at 10 K and 4 ps at 150 K. They find that coupling to both phonons and electrons is important, that for both mechanisms the rate increases with T, and that coupling to phonons is dominant at $T=150$ K. Their results are in rather good agreement with our experimental results, although direct quantitative comparison is difficult since their calculated damping rate is not separable into individual τ_e^{-1} and τ_{lat}^{-1} components. Clearly, there is need for further theoretical modeling to account for the adsorbate interacting with two heat baths of different temperatures.

Femtosecond visible pulses have been used to cause desorption [2] of CO from Cu(111) in less than 0.3 ps, and desorption [3,4] of NO from Pd(111) in less than 0.4 ps. From these short time scales, coupling of high T_e electrons ($T_e^{\text{max}}=3600$ K and 4500 K, respectively) to the reaction coordinate and not phonons must cause desorption. The mechanism is thought to involve excitation of CO^- and NO^- resonances by the very high T_e, followed by neutralization leaving the metal-adsorbate bond excited, leading to desorption [2–4]. The coupling time $\tau_e=5.1$ ps we find between ν_4 and T_e is much longer than the coupling times leading to these laser-induced reactions.

In conclusion, picosecond infrared pulses were used to follow the transient response of the $(\sqrt{2}\times\sqrt{2})R45°$ CO overlayer on Cu(100) following ultrafast excitation of the surface with 2.14 and 4.28 eV photons. Both the Fermi-Dirac hot electrons and the heated phonons are found to couple the frustrated translation mode on the picosecond time scale.

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