Femtosecond Laser-Induced Desorption of CO from Cu(100): Comparison of Theory and Experiment

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Desorption of CO from Cu(100) by femtosecond laser pulses was investigated using state and time-resolved techniques. The results are well described by two models based on frictional coupling between the CO and the substrate degrees of freedom: an empirical, 1D model, and recent, full-dimensionality, molecular dynamics calculations. [S0031-9007(96)01719-X]

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Femtosecond (fs) laser excitation causes apparently novel desorption dynamics for molecules on metal surfaces [1–6]. The systems studied to date display similar characteristics which include a nonlinear dependence of desorption yield (Y) on laser fluence (F), $Y \propto F^n$, with n reported in the range from 3 to 6.5, and a very short system response time, 0.3–1.8 ps. The qualitative interpretation of these characteristics was that the fs pulse briefly creates a very hot distribution of electrons (electron temperature $T_e \approx 4000$ K) which couples to the adsorbate to drive the desorption process. Two models representing nonadiabatic coupling in different limits have been used to quantitatively describe fs desorption. In DIMET (desorption induced by multiple electronic transitions) [1,2,5,7], the hot electrons couple to the adsorbate by exciting a transient negative ion resonance that decays to a neutral with vibrational excitation in the molecule metal bond; the adsorbate is subsequently re-excited before vibrational relaxation. Many such cycles may occur during the brief period of high T_e, with the bond accumulating enough energy to cause desorption. The second model invokes direct coupling between the electronic heat bath and the nuclear degrees of freedom via electronic frictions [5,7,8]. This frictional model also successfully describes the reverse process in which adsorbate vibrational excitation is damped by coupling to the metal free electrons [8].

To test current understanding of the fs desorption process, we have characterized the dynamics of the CO/Cu(100) system. In addition to the fluence dependent yield and system time response, we report the vibrational, rotational, and translational energy distributions of the desorbed CO. The CO/Cu(100) system has several distinct advantages over previously studied systems. At a coverage $\Theta = 0.5$ ML (1 ML $= 1.54 \times 10^{15}$ cm^2), only one binding site (top site) is occupied, and an ordered $c(2 \times 2)$ adlayer is formed. CO/Cu(100) has been characterized in great detail: The vibrational line positions and widths of the four adsorbate fundamental modes are known as a function of Θ and surface temperature T_s [9–12]; pump-probe measurements of the coupling times of two of these modes to the Cu electrons and phonons have been made [9,12]; and the Arrhenius parameters have been determined for first order desorption kinetics [13–15]. In addition, full-dimensionality trajectory calculations with electronic frictions derived from *ab initio* molecular orbital calculations have been performed for CO/Cu(100) [8,16]. The calculations yield lifetimes of the vibrational modes in agreement with experiment [8], and give the absolute yield, the fluence dependence of the yield, the time scale for desorption, and the rotational, vibrational, and kinetic energy of CO desorbed by fs laser pulses [16]. As described below, the trajectory calculations are in close agreement with our experiment. We have also compared our results to an empirical model which fits the data using *measured* Arrhenius desorption rate parameters and coupling times (frictions) between substrate electrons, phonons, and adsorbate vibrations. Comparison of experiment to both theories for the CO/Cu(100) system shows that frictional models account for many aspects of the data.

The surface diagnostics and procedures for preparing the $\Theta = 0.5$ ML ordered CO layer have been described [12]. All desorption experiments were performed with $T_s = 95$–100 K. The desorption laser pulses from a Ti:sapphire laser amplified at 10 Hz and frequency doubled to 400 nm were at normal incidence and had approximately a Gaussian spatial profile. The pulse duration measured by autocorrelation using surface second harmonic generation in reflection from $LiIO_3$ or GaAs was typically 160 fs full width at half maximum (FWHM). The laser spatial profile was constantly characterized by a CCD camera located at a position conjugate to the sample. We report the yield-weighted absorbed fluence $\langle F \rangle = \Sigma F^{n+1}/\Sigma F^n$, where n is the exponent in the experimentally determined power law dependence $Y \propto F^n$, and the sum is over the camera image. The CO which desorbed within $\pm 8°$ of the surface normal was detected by $2 + 1$ resonance enhanced multiphoton ionization (REMPI) via the $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ transition [17]. The probe laser was tuned to the CO ($v = 0$) bandhead for all measurements unless otherwise stated. The absolute desorption probability is estimated to be 3×10^{-4} per laser pulse at $\langle F \rangle = 46$ J/m^2 absorbed. Collisions between desorbing CO molecules are not believed to influence the measure-

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ments due to the small yield [18]. Y as a function of F was determined by fitting the first shot yield (from exponential fits to depletion curves) to ΣF^n. Over the range $\langle F \rangle = 20-50$ J/m^2, the CO yield is described by a power law with $n = 8 \pm 1$.

The kinetic energy distribution of CO (v, J) was determined from time-of-flight (TOF) spectra, where the CO^+ ion signal was recorded as a function of the time delay t_d between pump and probe pulses. The flux-weighted speed distribution is characterized by an average kinetic energy $\langle \mathrm{KE} \rangle$ and a reduced width $w = [2(\langle \mathrm{KE}^2 \rangle / \langle \mathrm{KE} \rangle^2 - 1)]^{1/2}$, which are $2k_BT$ and 1, respectively, for a Maxwell-Boltzmann distribution. We find for CO($v = 0$, $J = 6$) at an absorbed fluence $\langle F \rangle = 42$ J/m^2 that $\langle \mathrm{KE} \rangle = 0.037 \pm 0.003$ eV ($\langle \mathrm{KE} \rangle / 2k_B = 215$ K). $\langle \mathrm{KE} \rangle$ depends slightly on $\langle F \rangle$, increasing by about 30% as $\langle F \rangle$ increases from 25 to 55 J/m^2. $\langle \mathrm{KE} \rangle$ also varies with J, increasing by about 60% as J increases from 6 to 24; similarly w varies with J ranging from about 1.2 at low J to 1.0 at $J = 22$. $\langle \mathrm{KE} \rangle$ values for selected J sates for $v = 1$ were not significantly different from those in $v = 0$. For measurements requiring a fixed time delay between the pump and probe pulses, t_d was set to 20 μs corresponding to the intensity maximum of the TOF spectrum for CO($v = 0$, bandhead). The CO($v = 0$) Q-branch excitation spectrum and the derived population $P(J)$ distribution are shown in Fig. 1. $P(J)$ is slightly non-Boltzmann and characterized by a mean rotational energy $E_{\mathrm{rot}} = 0.019 \pm 0.002$ eV ($E_{\mathrm{rot}}/k_B = 225$ K). The population ratio CO($v = 1$)/CO($v = 0$) $= 0.098 \pm 0.017$ is characteristic of a Boltzmann distribution of vibrational states with $T_{\mathrm{vib}} = 1330$ K.

Information about the time for desorption was obtained from two-pulse correlation data. The 400 nm beam was split into two pulses of approximately equal energy. The time-delayed, recombined, orthogonally polarized beams were not collinear, but slightly displaced (+0.2°; −0.2°) from the surface normal. The inset in Fig. 2 shows CO desorption yield as a function of pulse/pulse time delay t_{pp} for CO($v = 0$, bandhead). The curve is approximately Gaussian with a FWHM of about 3 ps. Data for different values of $\langle F \rangle$ gave similar FWHM.

Our results may be interpreted by a simple empirical model for the coupling of a harmonic oscillator to two heat baths used to explain adsorbate vibrational excitation and relaxation following weak optical excitation [12]. The substrate electron and phonon bath temperatures, T_e and T_p, are calculated by the standard coupled diffusion equations [19]. The adsorbate-localized vibrational mode may exchange energy with both substrate heat baths according to $dU_v/dt = (U_e - U_v)/\tau_e + (U_p - U_v)/\tau_p$, where the energy $U_x = h\nu/(\exp^{h\nu/k_BT_x} - 1)$, T_x is the temperature of the designated heat bath (T_e, T_p, or T_v, for the vibrational mode), and τ_e and τ_p are coupling times between the oscillator and the electrons and phonons. Of particular interest are T_{ν_1} for the CO internal stretch, $\nu_1 = 0.259$ eV [9,12], which may be compared to the desorbed CO($v = 1$)/CO($v = 0$) population ratio, and T_{rc} for the reaction coordinate (rc) which determines the yield and is taken as the CO-Cu stretch, $\nu_2 = 0.043$ eV [11]. The model is solved for T_{ν_1} or T_{ν_2} with T_e and T_p as the driving terms, and the results are shown in Fig. 2. The first order desorption rate $R = k\Theta$ is calculated from an Arrhenius expression $k = A \exp[-E_a/k_BT_{\mathrm{rc}}(t)]$ and the yield is given by $\int R(t)\,dt$. For CO/Cu(100), information is available for all the parameters in the model (τ_e and τ_p for ν_1 and ν_2; A and E_a). For ν_1, time-resolved experiments determined $\tau_e = 2$ ps, while τ_p is very long (unimportant for the calculation) [9]. For ν_2, τ_e and τ_p have not been independently measured, although the sum $(1/\tau_e + 1/\tau_p)$ is constrained by the observed infrared

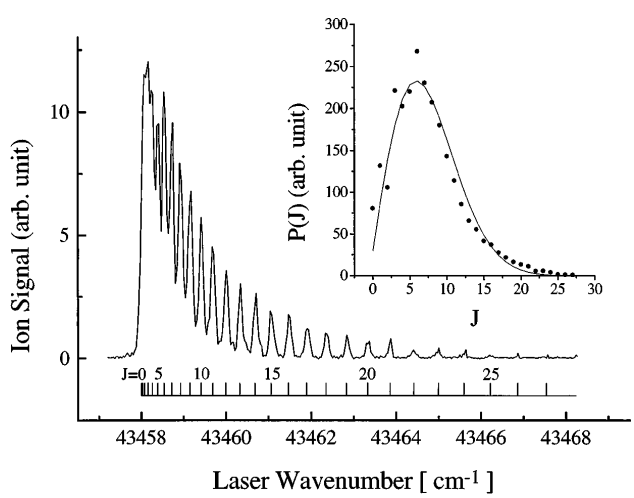

FIG. 1. REMPI signal for CO($v = 0$) at $\langle F \rangle = 46$ J/m^2. The inset shows the derived $P(J)$, corrected for the J dependence of the $\langle \mathrm{KE} \rangle$; the line indicates $P(J)$ for a Boltzmann distribution at an average energy of 0.019 eV.

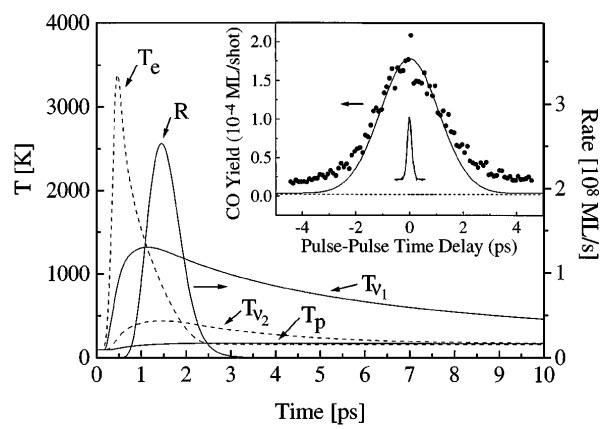

FIG. 2. T_e, T_p, T_{ν_1}, and T_{ν_2}, and the desorption rate R as a function of time calculated with the empirical model. The laser pulse is centered at 0.3 ps with a duration of 0.16 ps FWHM. Inset: Two-pulse correlation data (symbols) probing the CO($v = 0$, bandhead). The $\langle F \rangle$ for the combined pulses was 43 J/m^2. The inset solid line is the autocorrelation trace for the 400 nm pulses. The line through the correlation data is the prediction of the empirical model. The dashed line shows the sum of the slight yields from each pulse acting alone.

linewidth to be $\leq 0.5 \times 10^{12}$ s^{-1} [11]. The isosteric heat of adsorption for CO on Cu(100) is $\Delta H_{\mathrm{ads}} = 0.57$ eV for Θ in the range 0.1 to 0.5 ML [13]. Our temperature programmed desorption data at 1 K/s show a maximum at $T_s = 180$ K, consistent with $A = 2 \times 10^{15}$ s^{-1}. The one unknown parameter, τ_e/τ_p for ν_2, was taken to be 2 (i.e., $\tau_e = 6$ ps, $\tau_p = 3$ ps) to give an absolute desorption probability per pulse of 3×10^{-4} at $\langle F \rangle = 46$ J/m^2. The peak T_e and T_p are about 3400 and 170 K, while T_{ν_1} and T_{ν_2} peak near 1300 and 440 K, respectively (T_{rc} must be about 400–450 K to fit the desorption yield). The model predicts that over the experimental range, $Y \propto F^8$, in agreement with experiment. At the time of maximum R, the predicted T_{ν_1} is 1300 K, in agreement with the experimental value for the desorbed CO($v = 1$)/CO($v = 0$). It is plausible that the high frequency ν_1 will not be damped in the exit channel and so the population on the surface will be preserved into the gas phase. A similar model with coupling only to the electronic bath was applied to the ν_1 mode of NO following fs desorption from Pd(111) [5], with τ_e treated as an adjustable parameter. In order to account for the high excitation of ν_1, a τ_e much shorter than observed for CO/Cu(100) [12] was required.

The empirical model gives a two-pulse correlation curve, shown in the inset of Fig. 2, in good agreement with the data. The long time wings of the two-pulse correlation can be accounted for if different Arrhenius rate parameters are used, although the calculated yield power law is then too low. The 3 ps FWHM is greater than observed previously (0.6–1.8 ps) [2,6]. Since the model parameters are not known for these other systems, we cannot be sure of the sources of differences, or whether the present model would predict the other data.

The ability of the empirical model to reproduce $Y \propto F^n$ and the two-pulse correlation constrains $T_{\mathrm{rc}}(t)$, but does not prove that ν_2 rather than ν_3 (frustrated rotation, 0.036 eV) [11] or ν_4 (frustrated translation, 0.0045 eV) [10] best describes the reaction coordinate. For ν_4, coupling times of $\tau_e = 5.1 \pm 0.4$ ps and $\tau_p = 4.2 \pm 0.7$ ps have been reported [12]. If ν_4 is taken as the rc, values of τ_e and τ_p in the given range reproduce the absolute yield and the two-pulse correlation width, and give $n = 9$. For ν_3, independent values of τ_e and τ_p are not available but the ν_3 bandwidth requires $(1/\tau_e + 1/\tau_p) \leq 0.38 \times 10^{12}$ s^{-1} [11]. If $\tau_e = 6$ ps and $\tau_p = 5$ ps are chosen with ν_3 as the rc, the agreement with the experiment is also good. The agreement between the empirical model and the data is remarkable given that the parameters used in the simple model were measured at low T_s (under equilibrium conditions, or where the induced change in T_p and T_e was slight) and were taken to be independent of T_e, T_p, or T_v.

The empirical model makes no explicit prediction about the $\langle \mathrm{KE} \rangle$ or E_{rot} for CO. Unlike ν_1, the translations and rotations are basically classical and may exchange energy with each other, the phonons and other surface modes as CO desorbs. T_{rc} is calculated to be 440 K (which is likely to be the T of ν_3 and ν_4 also; see above) while T_p is about 170 K. Recall that the observed translational temperature is about 215 K and T_{rot} is about 225 K, which is suggestive of dynamical cooling with respect to the T_{rc}, as observed in many desorption systems [20]. No reasonable set of Arrhenius parameters for this system will give measurable desorption on a ps time scale at $T_{\mathrm{rc}} = 230$ K. The kinetic energy distribution was reported for CO thermally desorbed from Cu(100) by laser pulses of 15 ns duration [21]. As in our fs experiments, the distribution was almost Maxwell-Boltzmann with a translational temperature T_{trans} about 50% of the estimated $T_s = T_{\mathrm{rc}}$. An explanation for the cooling ($T_{\mathrm{trans}} < T_s$) is that the mean energy exchanged per Cu-CO vibrational period is significantly smaller than $k_B T_s$, so when CO finally achieves enough energy to desorb, its average excess energy is less than $k_B T_s$ [20]. Strong coupling between rotation and translation, and the finite time for energy transfer are thought to account for $T_{\mathrm{rot}} < T_s$ seen previously in desorption systems [20], and perhaps in the present experiment where $T_{\mathrm{rot}} < T_{\mathrm{rc}}$. By contrast, when a simple 1D DIMET model was applied to the $\langle \mathrm{KE} \rangle$ for O_2 following fs desorption from Pt(111) [22] it was found that the translational temperature was slightly *greater* than T_{rc}.

Insight into the microscopic physics leading to our observations may come from the work of Springer *et al.* in which coupling strengths were taken from *ab initio* calculations on CO-Cu clusters, and molecular dynamics simulations of CO desorption were performed in full dimensionality on realistic potential surfaces [16]. Table I summarizes the calculated [23] and experimental results. The energy partitioning in the desorbed CO, that is, the fraction of the total CO energy in translation, rotation, and vibration, is reproduced quite well by the simulations. The simulations for $F = 60$ J/m^2 and 100 fs pulses predict about a factor of two more total energy in the CO than is measured; the calculated CO energy is expected to be about 23% less at $F = 45$ J/m^2 [16]. The calculated yield exponent is slightly too small, while the two-pulse correlation width is close to that observed, and the simulations predict a broad (1–2 ps) distribution of exit times for molecules desorbing in a one-pulse experiment. Since the theory was not adjusted to fit the data, such agreement is extremely encouraging. Such theoretical studies present an opportunity to examine the desorption dynamics, thereby addressing experimental observations such as the dependence of the KE distribution on J state and laser fluence, and the slight non-Boltzmann character of the rotational and translational distributions and dynamical cooling.

In summary, we have determined the product state distributions, yield, and time scale for desorption of CO ($\Theta = 0.5$) from Cu(100) following fs laser excitation, an ideal system for comparing to theory. The results were compared to an empirical model, with coupling times and Arrhenius desorption rate constants taken from

TABLE I. Experimental and theoretical results for CO desorbed from Cu(100).

	Molecular dynamics[a] (60 J/m^2)[b]	Experiment (43–46 J/m^2)	Empirical model (46 J/m^2)
Yield (F^n)	$n = 5.6$[c]	$n = 8 \pm 1$	$n = 8.4$
ML/shot	2.5×10^{-3}	$\sim 10^{-4}$	3×10^{-4}
$\langle E \rangle_{\mathrm{rot}}$	0.034 ± 0.004 eV	0.019 ± 0.002 eV	
	395 K	225 K	440 K
$\langle E \rangle_{\mathrm{trans}}$	0.068 ± 0.006 eV	0.028 ± 0.002 eV[d]	
	525 K	215 K	440 K
$\langle E \rangle_{\mathrm{vib}}$	0.068 ± 0.007 eV	0.029 ± 0.006 eV	
	1940 K	1330 K	1300 K
Two-pulse correlation width	2–3 ps	3 ps	3 ps

[a]The frictions used in these calculations are smaller by a factor of two than those used in Ref. [16]. This makes $T = 0$ vibrational lifetimes calculated via molecular dynamics with electronic frictions [24] equal to the Fermi Golden Rule result (for the 6 atom cluster employed for the *ab initio* calculations to which the frictions were fitted [8]).

[b]To obtain reliable final state energies, the simulations were performed at higher fluence than the experiments to increase the desorption yield.

[c]This value of n was calculated using the stronger frictions in Ref. [16].

[d]To compare to the simulation results, the experimental $\langle E \rangle_{\mathrm{trans}}$ is calculated for a number density distribution rather than a flux distribution.

the literature. The data were also compared to recent full-dimensionality trajectory calculations with calculated couplings. Both the empirical model and the trajectory calculations agree quite well with the experimental results, indicating that for CO/Cu(100) frictional models account for the majority of the fs desorption data.

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