

Vibrational response of surface adsorbates to femtosecond substrate heating

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The transient response of the internal stretch vibration of CO molecularly adsorbed on Cu(111) has been measured following the impulsive (300 fs) excitation of electrons in the underlying metal substrate by a visible light pulse. It is proposed that the stretch vibration couples indirectly to substrate phonon and electron reservoirs via the frustrated translational surface mode. The couplings to the bulk electron reservoir with a rate $\gamma_e = 167(24)$ GHz, and to the bulk phonon reservoir with a rate $\gamma_L = 145(56)$ GHz were measured. The experiments represent an important step towards surface control of specific states of molecular adsorbates near their desorption threshold.

1. Introduction

The ultrafast dynamical response of molecular adsorbates on clean metal surfaces has been the subject of intense recent interest [1]. From a practical standpoint this work has been driven by the prospect of laser-induced surface transformations and chemical reactions [2]. From a more fundamental viewpoint, the first steps of simple photochemical processes at surfaces such as desorption, are of intrinsic interest and are incompletely understood [3]. In this contribution we probe the internal vibrations of an adsorbate molecule as a function of time following the impulsive excitation of electrons in the underlying metal substrate by a visible light pulse. The femtosecond excitation creates a unique environment for the surface adsorbate in which substrate electrons and phonons have dramatically different initial temperature distributions that equilibrate in approximately one picosecond. By studying the evolution of the molecular stretch vibrations during this time period, we have been able to deduce couplings between various degrees of freedom of the substrate metal and the surface adsorbate.

Hot electron-induced chemical processes, such as desorption from metals, have been previously ob-

served [4–7]. These experiments however, have generally relied on state-specific detection of molecules after desorption [5,6]. Few such experiments have directly probed molecules while they reside on the surface [4,7], and fewer still have detected molecules on a *state-specific* basis while they reside on the surface [7]. The present experiments represent an important step towards state-specific surface studies of molecular adsorbates near their desorption threshold. In this work we have chosen to study the internal stretch vibration of CO molecularly adsorbed to Cu(111). The CO is terminally bound as a $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer. A 300 fs visible light pulse (≈ 2 eV) excites the system, and a quasi-cw infrared (IR) probe pulse interrogates the stretch vibrations of the surface adsorbate. The time resolution of the measurement is provided entirely by the visible pulse, which pumps the system and time-gates the reflected IR pulse.

By contrast to previous work on Pt(111) [7], in the present experiment, a combination of shorter pulses ($3.3\times$), and the favorable properties of Cu(111), characterized by a much weaker bulk electron-phonon coupling constant ($\approx 20\times$), allow us to create a substantially greater ($\approx 20\times$) difference between the substrate electron and phonon temper-

atures. In addition the methods used in the present measurements are not affected by perturbed free-induction decay phenomena, and thus provide sensitivity to the *rising* as well as the falling portions of the temporal response^{#1}. These improvements enable us to resolve the response of the adsorbate vibration, and delineate the separate effects of electrons and phonons on the molecular heating processes. The experiments reveal that the stretch vibration couples indirectly to substrate phonon and electron reservoirs via a Brownian oscillator which is proposed to be the frustrated translational surface mode.

2. Experimental

A schematic of the apparatus is shown in fig. 1. The laser system [8,9] is based on a mode-locked Nd:YLF master oscillator whose frequency-doubled output synchronously pumps two dye lasers, and whose remaining fundamental radiation seeds a regenerative amplifier operating at 1 kHz. One of the two dye lasers is optimized to produce ≈ 200 fs visible pulses at 590 nm, and the other dye laser is optimized to produce narrow-band, tunable (580–610 nm), ≈ 30 ps pulses that are subsequently used to make probe IR light. The doubled output of the regenerative amplifier (1 mJ, 527 nm, 60 ps) provides pump energy for a series of dye amplification stages that are used to amplify either the femtosecond or picosecond visible light pulses. The amplified femtosecond pulses (3 μ J, 300 fs) are split into pump and gating pulses, while the amplified picosecond pulses (3 μ J, 30 ps) are difference-frequency-mixed in LiIO₃ with the remainder of the frequency-doubled regenerative amplifier output in order to produce tunable (1800–2100 cm⁻¹) quasi-cw, 10 nJ IR

^{#1} In a pump-probe experiment that utilizes short IR probe pulses (as in ref. [7]), the rise of the signal is determined by the dephasing time of the probed transition. This can be understood by considering the measured response following the probing of the system by a delta function IR pulse: in this case a perturbed free-induction decay signal of the vibrational transition is produced when the IR pulse arrives before the pump. On the other hand the risetime in our experiments is not very sensitive to the line-width of the vibrational transition as can be seen from eq. (1), with the present parameters.

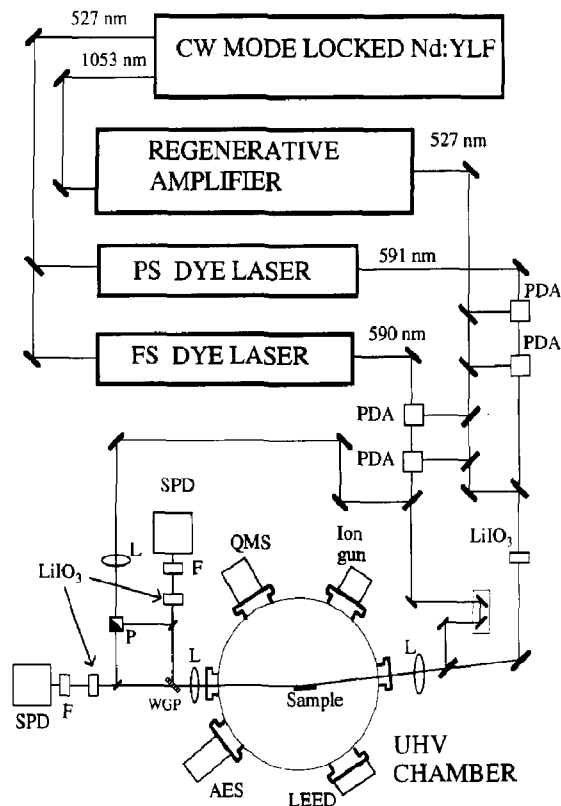


Fig. 1. Schematic of the apparatus. FS DYE LASER, synchronously pumped hybrid mode-locked dye laser (pulses ≈ 200 fs in duration); PS DYE LASER, synchronously pumped dye laser (pulses ≈ 30 ps); PDA, pulsed dye amplifier cells; F, spectral filter; SPD, silicon photodiode; L, lens; WGP, wire grid polarizer; P, polarizer; LEED, low-energy electron diffraction; AES, Auger electron spectrometer; QMS, quadrupole mass spectrometer.

pulses with a spectral fullwidth of 1 cm⁻¹.

The visible pump and IR probe pulses were made collinear, and then introduced into a UHV chamber [9] containing the Cu(111) crystal sample. The CO ($\sqrt{3} \times \sqrt{3}$)R30° ordered overlayer was prepared on the Cu surface by dosing 0.7 L at 95 K, and then annealing to 125 K. The laser pulses were focused onto the sample at an incidence angle of 85°. The visible beam was p-polarized, and the IR beam polarization adjusted to be 70% p-polarized and 30% s-polarized. The visible and IR beams were well approximated by Gaussian beams with waists of 90 and 176 μ m, respectively. Timing and overlap of the pulses were independently checked by detection of the transient reflectivity from a silicon wafer located in the chamber on the same sample manipulator.

Upon arrival at the surface the visible pulse penetrates $\approx 200 \text{ \AA}$ into the metal, simultaneously exciting electron-hole pairs which then equilibrate rapidly to produce an effective bulk electron temperature in considerable excess of the bulk phonon temperature [10–13]. The bulk phonon and electron temperature reservoirs equilibrate on a slower time scale. We have computed the time evolution for the latter process in our system using the standard coupled nonlinear differential equation approach [13]. In fig. 2 we present the results of this computation for Cu using our average visible pulse fluence. The shape of these curves depends on electron temperature-dependent thermal conductivities^{#2}, phonon and electron temperature-dependent specific heats^{#3}, the electron-phonon coupling constant^{#4}, and the source light distribution^{#5}. We see that the electron temperature reaches $\approx 400 \text{ K}$ dur-

^{#2} Following refs. [4,12], we take the electron thermal conductivity to be of the form $\kappa = 385T_e / (T_e + 1.37 \times 10^{-5}T_e^2) - \text{W/m K}$.

^{#3} The electron and phonon specific heat are assumed to be $C_e = 96.6T_e \text{ J/m}^3 \text{ K}^2$, $C_l = 2.26 \times 10^6 \text{ J/m}^3 \text{ K}$, respectively. These values are obtained from ref. [14].

^{#4} We use a value of $g = 1 \times 10^{17} \text{ W/m}^3 \text{ K}$ given in ref. [11].

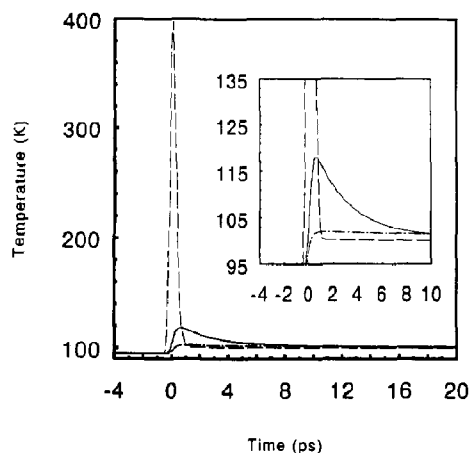


Fig. 2. Time evolution of the electron (dashed line), lattice (dot-dashed line), and adsorbate (solid line) temperatures at the surface of the Cu substrate for an average fluence absorption of 0.087 mJ/cm^2 . Inset: Same plot on an expanded vertical scale. Note, the adsorbate temperature was obtained using the best estimates for electron and phonon coupling rates γ_e and γ_l (see text for details).

ing the first picosecond, in considerable excess of the maximum lattice temperature (102 K). The two distributions equilibrate in $\approx 1 \text{ ps}$, and the lattice subsequently cools by thermal diffusion on a much slower time scale. We are, of course, interested in relating changes in CO stretch vibrations to the variations of these temperature distributions.

The IR probe frequency was tuned around the CO stretch resonance at 2074 cm^{-1} . Time-resolved detection was accomplished by difference-frequency-mixing reflected IR with delayed visible gate pulses (590 nm) after the sample [8,16]. The p- and s-polarized reflected IR beams were separately converted into 675 nm visible pulses. Two sets of matched photodiodes, amplifiers and spectral filters were used to detect these visible photons on a shot-by-shot basis. Since the adsorbed CO absorbs p-polarized light only, the s-polarized output provided a normalization signal every laser pulse. For a fixed IR frequency, the normalized differential reflectivity of the p-polarized probe IR pulse, with and without the visible (pump) pulse, was thus measured as a function of time.

The differential reflectivity of the reflected probe IR at time t , is of the form

$$G(\omega, t) = \text{Im} \left[i \int_{-\infty}^t dt' \exp \left(- \int_{t'}^t d\tau [S + \Delta S(\tau, t_p)] \right) - i \int_{-\infty}^t dt' \exp[-S(t-t')] \right], \quad (1)$$

where ω is the fixed probe IR frequency, $S = i(\omega_0 - \omega) + \Gamma_0$ is the complex frequency response of the adsorbate in the absence of perturbations, ω_0 and Γ_0 are, respectively, the unperturbed resonant frequency and damping of the oscillator, and $\Delta S(t, t_p) = i\delta\omega(t, t_p) + \delta\gamma(t, t_p)$ represents the time-dependent change in complex frequency of the oscillator as a result of external perturbations at time t_p . Eq. (1) is readily derived from the first-order equations of motion for the density matrix within the rotating wave approximation. Our measure-

^{#5} For a pump wavelength $\lambda = 590 \text{ nm}$ (see ref. [15]) we take the complex of index of refraction of Cu to be $n = 0.454 + i2.742$ at $T = 95 \text{ K}$. This enables us to compute the source light distribution in the metal.

ments can be fit using eq. (1) provided $\Delta S(t, t_p)$ varies slowly in time compared to oscillations of the incident field at frequency ω , and that the variation in substrate reflection is minimal. Our signals are quite small ($\approx 1 \times 10^{-3}$) so the first-order approximation is a good one. Because we were unable to detect any variation in *off-resonance* differential probe reflectivity, the substrate reflection condition is probably well satisfied too. We note however, that the model does not include visible-pulse-induced population transfer to higher energy states of the adsorbate. This effect, and the substrate reflection effect, may be more important at lower angles of incidence where the absorbed visible fluence is considerably larger. Studies of this nature are presently under way in our laboratories.

3. Results and discussion

We see from eq. (1) that the physics of the probed relaxation phenomena is entirely contained in the time variation of the complex frequency $\Delta S(t, t_p)$. In principle, any theoretical model explicitly relating substrate evolution to the complex frequency can be tested. A priori there exist many possible effects. Instantaneous electronic dephasing and lineshifts could result from ballistic electron impact with the adsorbate, or direct electronic excitation of substrate-adsorbate charge transfer states [17]. The high-frequency stretch mode could also couple *directly* to the substrate electron and phonon temperature reservoirs, or *indirectly* to the substrate electron and phonon reservoirs via other, low-frequency substrate-adsorbate vibrations such as the frustrated translational mode of the surface adsorbate. A brief inspection of the data in fig. 3 in the context of eq. (1) enables us to immediately rule out several of these mechanisms at the present level of excitation and signal-to-noise.

The differential reflectivity data are presented in fig. 3 as a function of time before and after the heating pulse. For this measurement, the probe laser was tuned 1 cm^{-1} higher in frequency than the center of the unperturbed CO lineshape (i.e. at $\approx 2075 \text{ cm}^{-1}$). Fig. 3a exhibits the rise of the disturbance, and fig. 3b exhibits the full time variation of the response. Qualitatively, the measurement possesses a fast rise

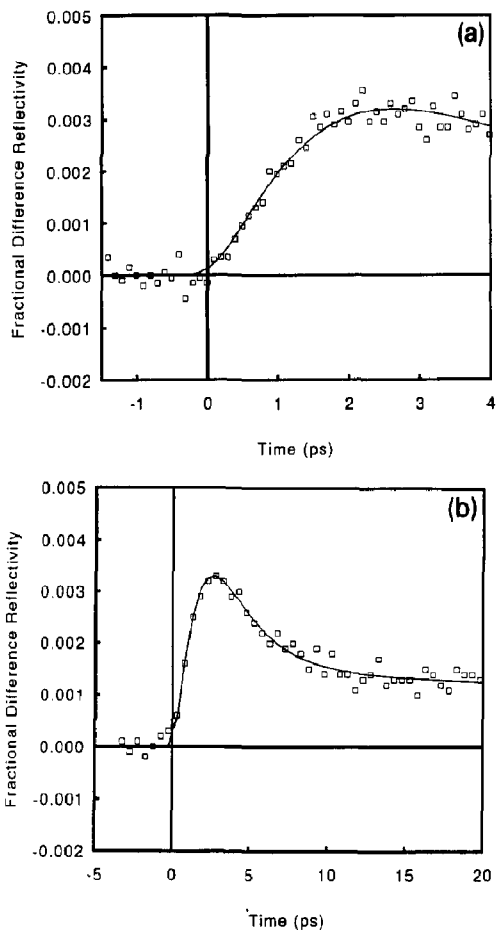


Fig. 3. (a) Rise of the fractional difference reflectivity signal ($\Delta R/R$) at 2975 cm^{-1} as a function of time after the visible heating pulse. The solid line is the best fit to the data using the anharmonic coupling model discussed in the text with our best estimates for the low-frequency reservoir coupling rates, $\gamma_e = 167 \text{ GHz}$ and $\gamma_L = 145 \text{ GHz}$. (b) Fractional difference reflectivity signal as a function of time over full time range. The solid line is same fit as in (a).

(subpicosecond), and then a relatively slow decay ($\approx 3.2 \text{ ps}$) to a baseline offset. Instantaneous electronic-heating-induced dephasing or spectral lineshifts may be observable. In such cases eq. (1) is used along with a step function model for $\Delta S(t, t_p)$, to show that the observed early time data can exhibit rapid variations if the spectral changes are large enough. These effects are quite similar in principle to Stark-shift-induced coherent transients [18]. In fig. 3a we see that the rise is easily resolved. Furthermore, our measurements utilizing probe fre-

quencies tuned to the *lower frequency* side of line center were of *opposite* signs at all times, and therefore could not have been brought about by rapid dephasing.

The time-integrated, long-time (5–15 ps), differential reflectivity of the IR beam as a function of probe frequency was obtained using longer, 3 ps pulses. This difference spectrum resembled the derivative of a Lorentzian lineshape, being positive at frequencies greater than the line center. Such a spectrum is indicative of the shifted Lorentzian that often arises in temperature-dependent studies of the vibrational lineshapes. There was a slight asymmetry due to simultaneous line broadening and shifting as well as the effects of finite visible and IR beam waists. Within the error of the present measurements, the CO spectrum, just after the substrate has equilibrated, clearly corresponds to the expectations for a shifted transition.

We now return to a quantitative analysis of the data in fig. 3 for the time regimes before the substrate has fully equilibrated. We consider two more plausible explanations for the observed behavior. In one scenario the CO stretch couples directly to the bulk phonons and electrons. In another scenario the CO stretch is anharmonically [19] coupled to a lower frequency surface-adsorbate vibrational mode, which in turn is coupled directly to the bulk phonons and electrons. A critical feature, crucial for both models concerns the manner by which a harmonic oscillator is coupled to a stochastic temperature reservoir. In our case there are two reservoirs (i.e. bulk electron and phonon) whose temperatures vary in different ways before equilibrating. Generally, if an oscillator with average energy U_{osc} characterized by a temperature T_{osc} (in the Boltzmann sense), is placed in contact with a thermal reservoir at temperature T_{R} , energy is exchanged until the oscillator acquires the reservoir temperature T_{R} . For a harmonic oscillator the time evolution of this process can be calculated explicitly and has a very simple form. The calculation depends only on the oscillator frequency, the average occupation of elementary excitations in the reservoir at the oscillator frequency, and the rate γ_{R} associated with the population relaxation between the lowest two oscillator energy levels in the presence of the reservoir. For this model, γ_{R} is temperature-independent, the elementary excitations in

the temperature reservoir are bosons, and we find that $dU_{\text{osc}}/dt = -\gamma_{\text{R}}[U_{\text{osc}}(t) - U_{\text{osc}}(\infty)] \approx -k_{\text{B}}\gamma_{\text{R}}(T_{\text{osc}} - T_{\text{R}})$ where k_{B} is the Boltzmann constant; the approximation prevails when the oscillator frequency is much less than $k_{\text{B}}T$. At lower temperatures the result has a similar form, $dU_{\text{osc}}/dt = -[\bar{n}(t) - \bar{n}(\infty)]\hbar\omega\gamma_{\text{R}}$, involving the time-dependent Bose occupation factor, $\bar{n}(t)$.

In our case the oscillator can couple to phonons or electron-hole pair fluctuations in the bulk. The occupation of both classes of elementary excitations are described by Bose distributions at the appropriate electron or phonon reservoir temperatures T_{e} and T_{L} respectively. We will assume that separate, temperature-independent electron (γ_{e}) and phonon (γ_{L}) transition rates exist for each reservoir so that for a harmonic oscillator

$$dU_{\text{osc}}/dt = \gamma_{\text{e}}[U(T_{\text{e}}) - U_{\text{osc}}] + \gamma_{\text{L}}[U(T_{\text{L}}) - U_{\text{osc}}], \quad (2)$$

where $U(T_{\text{e}})$ and $U(T_{\text{L}})$ are the energies the oscillator would have if it were separately in equilibrium with its electron and phonon baths. Eq. (2) enables us to compute the oscillator temperature, and thus the level occupation within the oscillator, as a function of time provided the time-dependence of T_{e} and T_{L} is known. We have calculated this temperature for the CO internal stretch vibration using the predicted temporal variation of electron temperature (see fig. 2), and the measured T_1 time of ≈ 1.2 ps^{#6} [21]. Since the CO stretch relaxation has been almost entirely attributed to electron-hole processes [21,22]^{#7}, and since the electron temperature is the only temperature in the problem that increases appreciably, this approach is well justified. We find however, that the induced population change is small ($< 2 \times 10^{-4}$), and there is as yet no evidence of this process in the data. In addition, as discussed above, we saw no evidence for direct (nearly instantaneous) temperature-induced spectral lineshifts or dephasing.

One simple model remains, whereby the CO internal stretch is anharmonically coupled to a lower

^{#6} The T_1 time can be inferred from temperature-dependent linewidth measurements [9,20]. For CO on Cu(100) T_1 has been measured directly [21].

^{#7} See ref. [23] for earlier theoretical estimates for these rates.

frequency surface adsorbate mode such as the frustrated translation. In this theory, often referred to as exchange theory [19,24], the complex frequency of the internal stretch depends explicitly on the average occupation of the low-frequency mode. The average occupation of the low-frequency mode, considered to be a Brownian oscillator, is controlled by its interaction with the bulk temperature reservoirs according to eq. (2). We have performed static FTIR measurements as a function of substrate temperature to confirm that this model adequately describes the temperature-dependent complex frequency shift over a limited range of temperatures (95–125 K). For example, within this temperature range the measured CO stretch lineshift varies linearly according to $\omega_{21} = (2078.4 - 0.052T) \text{ cm}^{-1}$. This variation indicates we are in the high-temperature limit of the exchange theory, that is, the low-frequency mode has an energy level separation considerably less than the thermal energy at 100 K as expected theoretically for the frustrated translation mode of the adsorbate. Since the frequencies of the frustrated rotation ($\omega_{\text{FR}} \approx 281 \text{ cm}^{-1}$) [25] and the Cu–CO stretch ($\omega_{\text{Cu-CO}} \approx 332 \text{ cm}^{-1}$) [20] are too high to account for the FTIR data, the frustrated translation is proposed to be the dephasing mode. For analysis of the optical response however, it is sufficient to obtain a phenomenological fit for $\gamma(T)$ and $\omega(T)$. It is not necessary to determine which mode causes the dephasing. Separate line broadening measurements were consistent with the lineshift measurements. Exchange theory predicts a quadratic high-temperature limit for the dephasing rate (linewidth) of the CO stretch transition, so we have used our best quadratic fit, i.e. $\gamma(T) = (4.854 + 0.000065T^2) \text{ cm}^{-1}$, in all subsequent analyses.

We have analyzed the data of fig. 3 using the anharmonic coupling model. In contrast to previous work [7] the entire temporal waveform provides relaxation information (see footnote 1). Briefly, the high-temperature version of eq. (2) was used to determine the temperature variation of the low-frequency oscillator, and the complex frequency of the CO stretch mode was obtained from the parameters derived from FTIR data. Our best estimates for the low-frequency reservoir coupling rates, $\gamma_e = 167(24)$ GHz and $\gamma_L = 145(52)$ GHz, give the solid lines shown in fig. 3, and give the adsorbate temperature

variation shown in fig. 2 (see solid line). The effects of finite laser spot sizes^{#8}, and finite pulse durations^{#9} were measurable, and were explicitly included in these fits. We note that γ_L is not as well determined as γ_e . The error in γ_L was obtained using γ_e and its error, along with the measured exponential decay rate (and its error) for data after 4 ps. The signal in this time regime is expected to decay exponentially at a rate of approximately the sum of γ_e and γ_L .

It should be noted that the expected response is sensitive to the assumed electron–phonon coupling constant g . This is important in light of the range of values for g that have been reported in the literature [11,12]. In fact we have found that our measurements can only be fit when g is in the range $(0.5\text{--}2.0) \times 10^{17} \text{ W/m}^3 \text{ K}$. Therefore we use the value of $1.0 \times 10^{17} \text{ W/m}^3 \text{ K}$ reported by ref. [11]. The measurements clearly reveal that the low-frequency vibrational mode, presumably the frustrated translational mode, couples to both electron and phonon bulk temperature reservoirs on a time scale of ≈ 6 ps. These times are of the same order of magnitude as recent temperature-dependent theoretical predictions for electron and phonon coupling to the frustrated translational mode of CO on Cu(100) [22,23], although theoretical predictions of stronger coupling to phonons than electrons is inconsistent with our results. The discrepancies may give evidence that phenomena associated with differences between surface geometry and electronic structure are important, or may be a result of missing physics in the models.

Before concluding, it is worthwhile to review the limitations of our model. The model assumes temperature-independent coupling rates, and essentially extrapolates static FTIR data obtained at ≈ 100 K to temperatures (albeit transient temperatures) in considerable excess of these values. The model treats the frustrated translation as an ideal harmonic oscillator, ignoring anharmonicities that may be important at high temperatures. The possible effects of other low-lying vibrational modes, particularly of surface

^{#8} For our spot sizes the peak fluence is $\approx 4 \times$ the average fluence. To account for this we convoluted eq. (1) with the appropriate Gaussian weighted distribution of fluences.

^{#9} Eq. (1) was convoluted with a 300 fs Gaussian pulse.

waves that may couple to or be involved in the frustrated translation motion, and of vibron motion arising from intermolecular coupling of the surface adsorbate to its nearest neighbors are not incorporated and need to be considered in more detail. On the other hand, the data clearly indicate that the model is a good starting point by which to understand these phenomena. Furthermore, the resolution and sensitivity of our measurements at *early times* may enable us to study more direct electronic-induced phenomena that are likely to arise at higher temperatures near the desorption threshold.

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