

Ultrafast Infrared Response of Adsorbates on Metal Surfaces: Vibrational Lifetime of CO/Pt(111)

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(Received 17 November 1989)

A picosecond time-resolved infrared technique has been used to measure the transient response of vibrationally excited CO adsorbed on the surface of a Pt(111) single crystal. Transient-bleaching signal decay is interpreted as giving T_1 for damping of vibrationally excited CO. Transient absorption is discussed in terms of transitions from the excited adsorbate band to overtone levels.

PACS numbers: 82.20.Rp, 68.35.Ja, 82.40.Js

Energy transfer at gas/solid interfaces is important in physical processes ranging from sticking and oxidation to catalysis and electronic materials processing. Presently, information on microscopic rates and mechanisms of vibrational energy dissipation has come from theory¹⁻⁶ or has been inferred from optical spectra.⁷⁻⁹ In this Letter, we report time-resolved measurements of the optical response associated with creation and relaxation of vibrationally excited adsorbate states on the surface of a metal single crystal. Experiments were done on the $c(4\times 2)$ overlayer observed at $\Theta=0.5$ monolayer (ML) for CO on Pt(111) at 150 K, a system for which extensive theoretical and experimental work has been reported.¹⁰⁻²⁰ An intense picosecond infrared laser pulse strongly excites the CO-stretching band of top-site CO, and a weak time-delayed probe pulse at the same frequency monitors the recovery of the surface absorption to its equilibrium value. This ir transient bleaching method has been used extensively to study vibrational energy relaxation times (T_1) and decay mechanisms in liquids,²¹⁻²⁴ for adsorbates on dielectric surfaces,²⁵⁻²⁷ and for CO chemisorbed on small metal particles.²⁸⁻³⁰ The present experiments provide the first direct measurement of the time scale of energy transfer in a vibrationally excited ordered monolayer bound to a metal single-crystal surface.³¹

The experiments were performed in an ultrahigh vacuum chamber (base pressure $< 10^{-10}$ Torr) equipped for Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), temperature programmed desorption (TPD), and ion sputtering. A 15-mm-diam \times 3-mm-thick Pt(111) disk, aligned to $\pm 0.1^\circ$ using an x-ray diffractometer before polishing, was mounted on an x, y, z, θ sample manipulator which was liquid-nitrogen cooled ($T_{\min}=115$ K) and heated by electron bombardment ($T_{\max}=1300$ K). CaF_2 windows permitted optical radiation to propagate through the chamber while reflecting from the crystal face at near-glancing incidence ($\theta_i=87^\circ$). The sample was cleaned by oxidation to remove carbon impurities and Ar^+ sputtering to remove Ca and Si impurities,¹²⁻¹⁴ and routinely monitored using AES.³² Adsorbed CO layers were character-

ized using LEED, TPD, and Fourier-transform infrared reflection-absorption spectroscopy (IRRAS). The observed ordered overlayers and TPD features were consistent with those reported in the literature for surfaces with low (< 0.01) defect and step densities.¹²⁻¹⁵ The temperature and coverage dependence of the CO/Pt(111) ir absorption features in the 1800–2200- cm^{-1} spectral region were in good agreement with published data for samples of normal CO isotopic abundance.^{15,17,18} The Pt sample temperature and CO coverage were fixed at 150 K and 0.5 ML for all measurements reported here.

Single-color time-resolved infrared-pump-infrared-probe measurements were performed using infrared pulses generated by nonlinear difference frequency mixing of two visible pulses in a LiIO_3 crystal.^{29,30} The visible pulses were derived from two 82-MHz synchronously pumped dye lasers with pulse durations (FWHM) of 3.5 ps at 15784 cm^{-1} and 3.3 ps at 17889 cm^{-1} , amplified at 20 Hz to energies of 400 and 750 μJ , respectively. The resultant ir pulses at 2105 cm^{-1} had a measured bandwidth of 4 cm^{-1} (FWHM) and a temporal duration of $t_p=3.8$ ps (FWHM measured by autocorrelation in LiIO_3), with average pulse energies of 10 μJ . The average energy of the p -polarized ir pump beam was varied from 2.8 to 6.5 μJ with attenuators. A fixed fraction of each ir pulse ($\approx 3\%$) formed the ir probe pulse, which was optically delayed relative to the pump and polarized at 45° with respect to the horizontal surface normal. The laser pulses are focused onto the crystal with a 30-cm focal-length lens. Pump and probe beams are parallel but displaced by 1 cm at the lens (beam radii $w=3$ mm at this point). The plane of the two beams bisects the surface at an angle 87° from the surface normal. Thus, they overlap on the crystal at the focus with the same angle of incidence ($\theta_i=87^\circ$) and beam waist ($w_0=0.16$ mm). Relative intensities of the reflected p and s components of the probe beam (I_p/I_s) were measured by a pair of InSb detectors with wire-grid polarization analyzers. In the absence of the pump, this ratio is denoted $(I_p/I_s)_0$. In the pump-probe experiment, the transient optical response $\beta=(I_p/I_s)/(I_p/I_s)_0$ was re-

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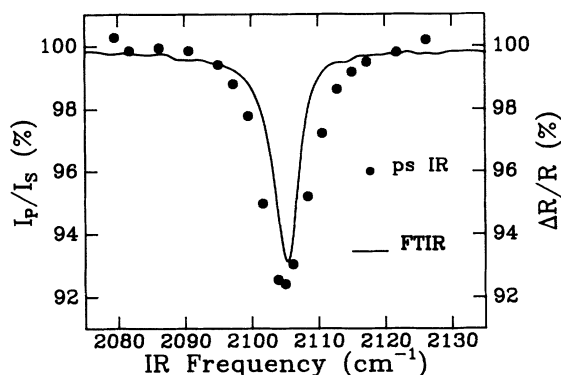


FIG. 1. Solid line is the Fourier-transform IRRAS of CO/Pt(111) at $\Theta=0.5$ ML and $T=150$ K (right-hand axis). Solid circles show IRRAS obtained under the same sample conditions, but monitoring the p and s components of the picosecond laser pulse (left-hand axis). The observed 4-cm^{-1} width of the 2105-cm^{-1} top-site absorption is consistent with the convolution of the 2.0-cm^{-1} Fourier-transform ir (FTIR) bandwidth and a 3.5-cm^{-1} (FWHM) sample absorption.

corded as a function of the pump-probe delay time, t_D .

Figure 1 shows a spectrum obtained by recording $(I_p/I_s)_0$ as the frequency of the picosecond ir pulses is tuned across the CO/Pt(111) absorption band. Also shown in Fig. 1 is the spectrum obtained under identical conditions by Fourier-transform IRRAS with 2.0-cm^{-1} resolution, showing an absorption maximum of $\Delta R/R=7\%$ at 2105 cm^{-1} with a FWHM of 4.0 cm^{-1} . The picosecond ir spectrum reflects the additional spectral width due to the 4-cm^{-1} bandwidth of the ir pulses.

Figure 2(a) depicts the transient optical response, $S=\ln\beta(t_D)$, when the picosecond radiation is tuned to 2109.4 cm^{-1} , 4.4 cm^{-1} higher in frequency than the Fourier-transform IRRAS maximum. The transient signal, which corresponds to a pump-induced increase in reflectivity (bleach), is shown along with the ir pulse autocorrelation. The surface signal $S(t_D)$ is significantly broader in time than the laser autocorrelation function, $G(t_D)=\text{sech}^2(1.762t_D/t_p)$. In order to extract a numerical value for the vibrational relaxation rate,³³ the data S were fitted by the convolution of G and R , where $R(t_D)=\exp(-t_D/\tau)$, and a nonlinear least-squares routine determined the best-fit τ . The data were also antisymmetrized (to eliminate coherent pulse coupling artifacts sometimes observed in one-color pump-probe experiments³⁴) before being fit. Since autocorrelations were not determined simultaneously with sample decay data, the sensitivity of the deduced τ to uncertainties in t_p and the position of $t_D=0$ was tested by fitting the data assuming slightly different values for these parameters. Analysis of direct and antisymmetrized convolutions for the data in Fig. 2(a) and six other data sets obtained from adlayers prepared on different days gave $\tau=4.9\pm 1.6$ ps for the mean value and standard deviation (1σ) in the best-fit τ ; the least and greatest of the fitted τ values were $\tau=2.1$ and 8.4 ps, respectively.

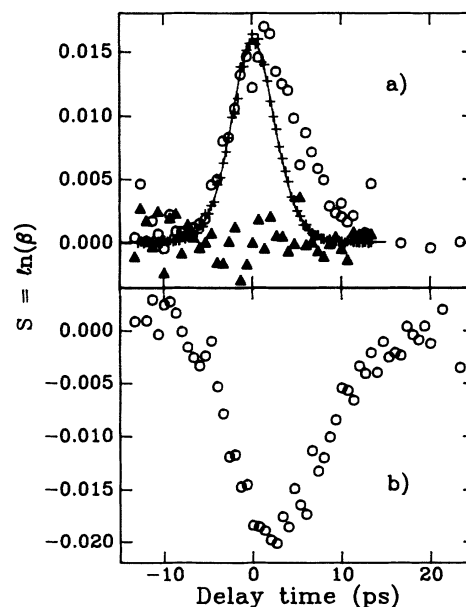


FIG. 2. Transient change in reflectivity $S=\ln\beta$ as a function of pump-probe time delay t_D for CO/Pt(111) at $\Theta=0.5$, $T=150$ K. (a) Open circles show sample bleaching following excitation at $\nu=2109.4\text{ cm}^{-1}$ ($3.6\text{ }\mu\text{J}$). Solid triangles show null sample response for $\nu=2125\text{ cm}^{-1}$, far from any CO absorption. Plusses give laser autocorrelation (height is arbitrary); the line through points gives the best fit by a sech^2 laser profile with $t_p=3.8$ ps. (b) Transient decrease in reflectivity following excitation at $\nu=2100.6\text{ cm}^{-1}$.

Experiments conducted at this frequency on a surface free of CO, or on a 0.5-ML CO covered surface with the laser tuned 20 cm^{-1} to higher frequency [see Fig. 2(a)], did not indicate any transient response greater than $|S|=0.005$. These null results lead to two important conclusions regarding the transient in Fig. 2(a). First, the signal is not dominated by a pump-induced temperature jump. Most of the incident $5\text{-}\mu\text{m}$ radiation absorbed by either clean or CO-covered Pt is absorbed directly by the substrate. From the optical constants and heat capacity of Pt, a peak temperature rise $\Delta T=10$ K is calculated for our pump-laser fluence.³⁵ This ΔT should give a peak transient decrease in reflectivity $S\approx 0.005$, decaying on the time scale of about 100 ps .³⁶ Second, the transient is clearly a resonant effect associated with vibrational excitation of adsorbed CO. The sign and magnitude of the transient-bleaching signal in Fig. 2(a) are consistent with the recovery time of a two-level system where the excited state corresponds to $\text{CO}(v=1)$. Similar bleaching-decay curves have been observed for CO modes in metal carbonyl compounds^{22,23,27} and for OH stretching modes of alcohol and silanol molecules.²¹ In those systems, because of anharmonicity, the $v=1$ states absorb little of the probe, thus causing a bleach which decays exponentially with the $v=1$ population decay time, T_1 . This is the simplest and most likely interpretation of the bleaching transient reported here, i.e.,

$\tau = T_1$.

The deduced value of T_1 should be viewed as a preliminary result for several reasons. For the CO/Pt(111) system there is not a well-tested model for the transient infrared optical response to short pulses and strong resonant excitation. While the data do not prove that the response is a simple exponential, the signal-to-noise ratio (S/N) is not sufficient to observe more complex decay behavior. Even if the exponential response approximation is adequate, deconvolution of the sample response from a laser pulse of approximately the same duration (4.9 vs 3.8 ps) can be done with complete confidence only when the S/N is much higher than for the present data ($S/N \approx 10$). Implicit in the deconvolution³⁴ is the assumption of a sample response S linear with laser intensity I . Although the bleaching signal increased with pump-laser fluence, the variation (2.6–6.5 μJ) does not severely test the scaling of S with I .

Interpreting the data in Fig. 2(a) as giving $T_1 = 4.9 \pm 1.6$ ps, one may compare T_1 to the ir absorption spectral bandwidth, to previous T_1 measurements in other systems, and to possible damping mechanisms. Our Fourier-transform IRRAS spectra agree with previous studies^{15,17,18} showing the low-temperature (< 200 K) bandwidth for $c(4 \times 2)$ top-site CO is $\Delta\nu$ (FWHM) = 3.5 cm^{-1} . Using the uncertainty principle for a Lorentzian band shape $\{T_1 = [2\pi c \Delta\nu (\text{cm}^{-1}, \text{FWHM})]^{-1}\}$, this corresponds to a decay time of $T_1 = 1.5$ ps, which is less than T_1 deduced from our time-resolved measurements. Apparently there are dephasing processes (including, perhaps, inhomogeneities) which broaden the spectrum beyond the T_1 width. The value $T_1 = 4.9 \pm 1.6$ ps is similar to the decay time²⁹ for CO on Pt particles (≈ 20 Å diameter) for which $T_1 = 7 \pm 1$ ps for $100 < T_s$ (K) < 400 . T_1 for CO on platinum surfaces is much too short to be due to multiphonon relaxation to low-frequency adsorbate modes (e.g., Pt-CO stretch^{16,18} $\nu = 467$ cm^{-1} or Pt-CO bend²⁰ $\nu = 411$ cm^{-1}) or substrate modes ($\Theta_D = 195$ cm^{-1}). Relaxation to such low-frequency modes (≥ 5 quantum relaxation) is inefficient and has been measured^{22,23,30} to take at least several hundred ps for CO($\nu = 1$) modes of metal carbonyl molecules. Vibrational damping due to coupling with substrate electron-hole pairs has been proposed as a mechanism to explain the low-temperature bandwidths for high-frequency modes of adsorbates on metals.^{1,3-9} Energy relaxation by this mechanism is predicted to be rapid and essentially temperature independent, consistent with our measurements of T_1 for CO on Pt particles, and the fast decay for CO/Pt(111).

Figure 2(b) contains data obtained when the laser is tuned to 2100.6 cm^{-1} , 4.4 cm^{-1} below the absorption maximum. A pump-induced decrease in reflectivity (i.e., transient absorption, $S < 0$) is observed on a time scale comparable to that shown in Fig. 2(a). These data are suggestive of transient absorption effects observed for

metal carbonyls.^{23,30} In those molecules, optical density associated with the $\nu_1 \rightarrow 2$ transitions is anharmonically shifted from the $\nu_0 \rightarrow 1$ transitions such that for pulses tuned below $\nu_0 \rightarrow 1$, the probe measures transient absorption due to resonant ($\nu_1 \rightarrow 2$) interaction with the $\nu = 1$ population. A rate-equation model²³ which treats CO/Pt(111) as a multilevel system, e.g., CO($\nu = 0, 1, 2, 3$), reproduces both the $S > 0$ and $S < 0$ transients in Fig. 2, consistent with $T_1 = 5$ ps for CO($\nu = 1$), the known laser parameters, and the $\nu_0 \rightarrow 1$ absorption profile of CO/Pt(111). However, the model requires the frequency shift between the $0 \rightarrow 1$ and $1 \rightarrow 2$ to be $\Delta\nu_s = 4$ cm^{-1} , which is smaller than the anharmonic frequency shift for isolated gas-phase CO ($\Delta\nu_s = 27$ cm^{-1}), but is within the range reported for strongly coupled anharmonic metal carbonyl modes ($3.0 \leq \Delta\nu_s \leq 12$ cm^{-1}).³⁷

The small $\Delta\nu_s$ is not readily derived from a simple picture of dispersion of the modes of the coupled CO oscillators. A model calculation³⁸ of the dispersion $\omega(\mathbf{k})$ for the positively dispersive CO($\nu = 1$) band and the CO($\nu = 2$) two-phonon bound states indicates that at the band center the $1 \rightarrow 2$ transition is lower in frequency than the $0 \rightarrow 1$ by $\Delta\nu_s = 2x_M + \lambda/2 + \lambda^2/8x_M$, where x_M is the Morse anharmonicity of a CO bond and λ is the coupling constant between two equivalent CO adsorbates ($x_M \approx 12$ cm^{-1} and $\lambda \approx 20$ cm^{-1} in metal carbonyls³⁹). At the band edge $\Delta\nu_s = 2x_M$, so that throughout the band $\Delta\nu_s \geq 2x_M$. Therefore the $S < 0$ response in Fig. 2(b), which seems to require $\Delta\nu_s \approx 4$ cm^{-1} , is difficult to reconcile with this simple model.

A realistic model of the present optical experiments, which must include CO anharmonicity, CO-CO coupling, exchange dephasing by other modes, electron-hole-pair damping, strong adsorbate excitation, and delocalization within excited-state bands, has not yet been formulated. Similarly, many aspects of adsorbate-adsorbate coupling are absent from the models currently used to interpret vibrational spectral bandwidths.¹⁻¹¹ For instance, excited-state-excited-state scattering (known to cause vibrational up-pumping for CO molecules⁴⁰⁻⁴³) and intraband relaxation may influence the transient spectral response, as could excitation transfer to naturally occurring ¹³CO adsorbates or CO in bridge sites, or excitation trapping by impurities, steps, or defects. Future time-resolved infrared experiments, with improved time resolution and independent pump and probe wavelengths, promise to directly address these questions of the vibrational dynamics of adsorbed layers.

This work was supported in part by the Air Force Office of Scientific Research. One of us (J.D.B.) acknowledges support through a National Research Council-National Institute of Standards and Technology postdoctoral research associateship.

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