

## Infrared Fluorescence from a Monolayer of CO on NaCl(100)

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Infrared fluorescence has been observed from a monolayer of  $^{13}\text{C}^{16}\text{O}$  on NaCl(100) following vibrational excitation of its fundamental absorption band with a pulsed CO gas laser. Direct time-domain measurements of the fluorescence reveal a lifetime of 4.3 ms. Since fluorescence occurs in the overtone region from high vibrational states, these results demonstrate that energy can be stored in the adsorbate long enough to allow vibrational up-pumping between neighboring molecules. It is suggested that the primary channel for CO vibrational relaxation is  $\Delta v = -1$  transfer to phonons of the NaCl substrate.

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Direct time-domain measurements of vibrational relaxation have only recently been extended to adsorbates on metallic<sup>1,2</sup> and semiconductor<sup>3</sup> single-crystal surfaces. In this Letter we expand this list to include vibrational relaxation on a single-crystal insulator surface. Our system is CO on NaCl(100).

In previous studies<sup>4,5</sup> we have estimated the rate of vibrational energy flow from the CO-chemical-bond mode to the (100) surface of NaCl single crystals to be of the order of  $10^3 \text{ s}^{-1}$ . Following pumping of the adsorbate with a pulsed CO laser, this value was obtained indirectly when lifetimes of the  $\Delta v = -2$  overtone fluorescence from high vibrational states of multilayer CO were determined systematically and extrapolation was made for the relaxation rate of the first layer. Experiments to measure monolayer fluorescence were deemed feasible since the surface relaxation rate is only about 2 orders of magnitude higher than the CO radiative rate.<sup>6</sup>

In our laboratory we now have successfully observed infrared fluorescence emanating from an optically excited monolayer of CO on the NaCl(100) surface. Although infrared emission from CO on Ni(100) was first detected using a liquid-helium-cooled spectrometer,<sup>7</sup> this work significantly differs from ours. In the former experiments, the crystal and adsorbate were maintained at equilibrium conditions and no dynamic information was revealed since blackbody radiation was monitored. Moreover, since the fluorescence we observe is from *overtone* transitions our results demonstrate that highly excited vibrational levels of the adsorbates can be generated when the molecules are weakly bound to a passive substrate. This implies that vibrational up-pumping through efficient dipole-dipole coupling can take place within one layer of aligned molecules.

Details of our experimental apparatus, optical layout, and procedures for preparing the CO monolayer have been given elsewhere.<sup>4,5</sup> Briefly, the experiments were conducted on the (100) surfaces of two NaCl single crystals mounted in a UHV chamber which was equipped with a quadrupole mass spectrometer. The total base pressure of the evacuated system was  $8 \times 10^{-10}$  mbar and was mainly due to  $\text{H}_2$  and inert gases. The crystals

for this work are identical to our earlier samples.<sup>4,5,8,9</sup> They were air cleaved and their interrogated surfaces contacted nothing but air, which was later baked away at 380 K under vacuum. Low temperature for the crystals was achieved by gas flow from a liquid-helium reservoir to their supporting copper cryostat work surface. Before admitting CO into the chamber, the gas was carefully purified with Ascarite and magnesium perchlorate to remove the components of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the sample. The monolayer was then prepared by maintaining a sufficient pressure of CO in the UHV chamber to ensure equilibrium between the gaseous and adsorbed phases. At 55 K or lower temperatures, the adsorbate was characterized using a Fourier-transform infrared spectrometer. The spectral resolution for the experiment was  $0.11 \text{ cm}^{-1}$  and frequency was measured to have an accuracy of  $\pm 0.01 \text{ cm}^{-1}$ . The quality of the surfaces was assessed by comparing the high-resolution polarized infrared spectra with previous spectra of CO on clean NaCl(100). In this experiment, a monolayer of  $^{13}\text{C}^{16}\text{O}$  (99%  $^{13}\text{C}$ , 99.5%  $^{16}\text{O}$ ) was prepared in order to match the output of a CO gas laser. At 22 K the vibrational absorption band of  $^{13}\text{C}^{16}\text{O}$  on NaCl(100) is centered at  $2107.40 \text{ cm}^{-1}$  with a full bandwidth at half maximum (FWHM) of  $0.15 \text{ cm}^{-1}$ , as shown in Fig. 1.

A Q-switch CO gas laser operated at a pulse rate of 25 Hz was used as the excitation source.<sup>4,5</sup> Unwanted high- $v$  transitions ( $v > 6$ ) of its output were limited by a narrow-bandpass interference filter. Laser emission from several rotational levels from  $v=1$  to  $v=6$  bathed the monolayer. The principal exciting CO laser line was  $P_{1 \rightarrow 0}(9)$  at  $\tilde{\nu} = 2107.42 \text{ cm}^{-1}$ , which overlapped the adsorbed-CO band center to within  $0.02 \text{ cm}^{-1}$ . This line was measured to have an energy of  $25 \mu\text{J}/\text{pulse}$  with a pulse duration ( $t_p$ ) less than  $5 \mu\text{s}$ . During the excitation experiments, the laser light was 60%  $E_p$  polarized to match the perpendicular orientation of CO on the surface.<sup>10</sup> The incident angle ( $\theta_p$ ) was near  $40^\circ$  with respect to surface normal and the irradiated area was approximately  $0.01 \text{ cm}^2$ . Flux for the  $2107.42\text{-cm}^{-1}$  photons is therefore estimated to be  $F_p = 7 \times 10^{21}$  photons  $\text{cm}^{-2}\text{s}^{-1}$ . We have measured elsewhere<sup>6</sup> the infrared

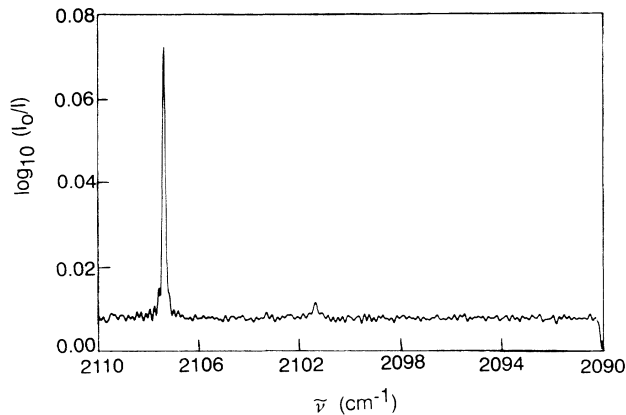


FIG. 1. Vibrational spectrum of a monolayer of  $^{13}\text{C}^{16}\text{O}$  on NaCl(100) at 22 K. The prominent feature is located at  $2107.40\text{ cm}^{-1}$  with a bandwidth (FWHM) of  $0.15\text{ cm}^{-1}$ . The small satellite at  $2101.4\text{ cm}^{-1}$  is associated with heterogeneous sites on the surface as discussed in Ref. 8. The inverted feature at  $2090\text{ cm}^{-1}$  is due to incomplete cancellation of atmospheric water absorption between sample and background scans.

cross section of  $^{13}\text{C}^{16}\text{O}$  on NaCl(100) and found a value of  $\sigma_z = 3.0 \times 10^{-17}\text{ cm}^2\text{ molecule}^{-1}$  along the CO molecular axis. By taking into account our experimental arrangement, the pumping rate in this experiment is calculated to be  $k_p = \sigma_z F_p \sin^2 \theta_p = 9 \times 10^4\text{ s}^{-1}$ . Compared to the most efficient channel of surface relaxation that was previously estimated to have a rate of  $\approx 10^3\text{ s}^{-1}$ , this pumping is much faster than any relaxation during the excitation. Each pulse is thus able to pump a fraction of  $[1 - \exp(-k_p t_p)]/2 = 0.2$  of the molecules to the first excited state, provided that the intermolecular transfer between CO molecules is not present.

In order to avoid the interference of strong scattered laser light in the CO fundamental region, we collected overtone fluorescence and filtered out the exciting laser light with a plate of infrared-grade fused quartz. Using the same optical scheme as before,<sup>4,5</sup> except with the monochromator being removed, the total fluorescence signal was detected by a liquid-nitrogen-cooled InSb detector. The decay signals from the detector were then passed to an amplifier (with a gain of 1000) and finally to a FabriTek 1074 signal averager which added 50000 scans in 40 min. Figure 2 shows the results of our time-domain measurements of overtone fluorescence from the excited monolayer of  $^{13}\text{C}^{16}\text{O}$  on NaCl(100) at 22 K. The fluorescence decay can be fitted with a simple exponential function, as indicated by the solid curve. The lifetime of this relaxation is found to be  $\tau_{\text{obs}} = 4.3 \pm 0.4\text{ ms}$ .

We have been careful to eliminate the possibility that the fluorescence comes from any source other than the excited CO monolayer on NaCl(100). Before admission of CO to the UHV chamber no infrared emission was observed. The fluorescence does not come from residual

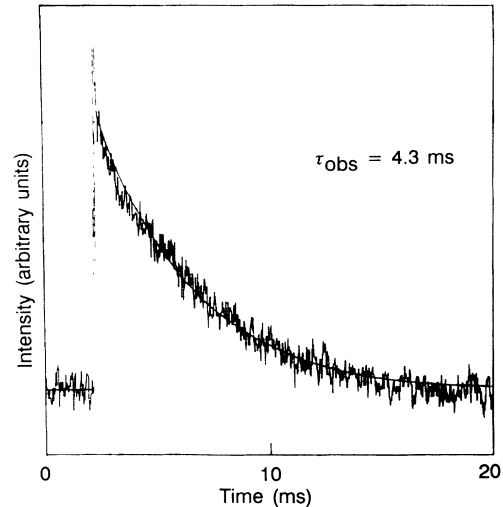


FIG. 2. Time evolution of infrared fluorescence emanating from a monolayer of  $^{13}\text{C}^{16}\text{O}$  on NaCl(100). The fluorescence decay can be fitted with a simple exponential function (solid curve) and has a time constant of 4.3 ms.

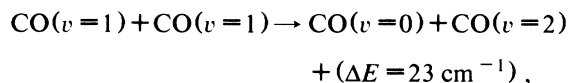
gaseous  $^{13}\text{C}^{16}\text{O}$  in the chamber since its rovibrational transitions are not matched by the lines of the  $^{12}\text{C}^{16}\text{O}$  laser. Furthermore, the fluorescence does not radiate from the gas-phase CO after collision with the excited adsorbed layers. At 22 K, the partial pressure of  $^{13}\text{C}^{16}\text{O}$  was measured by the mass spectrometer to be  $5 \times 10^{-12}\text{ mbar}$ .<sup>6</sup> This pressure is so low that a CO molecule strikes a surface site only once every 140 h. In this experiment we have carefully controlled CO flow to prevent the formation of multilayers.<sup>11</sup> Condensed multilayers, whose absorption bands are centered around  $2092\text{ cm}^{-1}$ ,<sup>5</sup> are not detected in the infrared spectrum of Fig. 1. The weak feature at  $2101.4\text{ cm}^{-1}$ , present even when multilayers are intentionally generated by techniques described elsewhere,<sup>11</sup> is associated with defects on the NaCl surface.<sup>8</sup> Therefore we also rule out the possibility of fluorescence from excited multilayers.

In another set of measurements, a short-pass interference filter was placed in front of the InSb detector indicating that much of the fluorescence was in the region  $4200\text{--}3400\text{ cm}^{-1}$  and thus originated from  $v=15$  to  $v=2$  levels of  $^{13}\text{C}^{16}\text{O}$ . What is the origin of the overtone fluorescence?

Pumping from laser lines other than  $P_{1-0}(9)$  is possible. Our previous measurements show that the spectroscopic constants of CO are little affected by adsorption on NaCl(100). Vibrational frequencies of adsorbed  $^{12}\text{C}^{16}\text{O}$ ,<sup>11</sup>  $^{13}\text{C}^{18}\text{O}$ ,<sup>4,5</sup> and  $^{13}\text{C}^{16}\text{O}$  of Fig. 1 are within 1% of their gas-phase values<sup>12</sup> and consistent with a similar small change in the anharmonicity constant  $\omega_e x_e$ .<sup>13</sup> Similar small changes are also reported in the solid  $\alpha$ -CO (Ref. 14) spectroscopic constants. Using  $\omega_e x_e = 12.7\text{ cm}^{-1}$  for  $^{13}\text{C}^{16}\text{O}$ ,<sup>12</sup> we calculate the  $v=1$  to  $v=2$  transition to be near  $2082\text{ cm}^{-1}$ . However, this

value is the transition when the monolayer consists of a single  $v=2$  excitation in the presence of  $v=1$  molecules: an exciton state.<sup>8</sup> As we have estimated earlier, each laser pulse can pump about 20% of the molecules to the first excited state. Thus coherent motions of the adsorbates will be interrupted during the excitation. The absorption band of  $v=1$  to  $v=2$  is therefore expected to be redshifted by  $\approx 1 \text{ cm}^{-1}$  and its bandwidth to be broadened to a FWHM of  $\approx 0.5 \text{ cm}^{-1}$  as our impurity-doping measurements have shown.<sup>9</sup> This allows the band profile to encompass the laser line of  $P_{2-1}(10)$  at  $2081.26 \text{ cm}^{-1}$ , and the adsorbate may further be up-pumped to the  $v=2$  vibrational state. This type of excitation may also take place to other vibrational levels. At this stage we are not certain to what extent other high-transition laser lines are responsible for the observation of overtone fluorescence. However, our laser excitation source is filtered for energies below  $1950 \text{ cm}^{-1}$ , so direct pumping beyond  $v=7$  is not possible.

The generation of overtone fluorescence from levels above  $v=1$  can also be attributed to vibrational up-pumping between CO molecules within the monolayer. Through a series of reactions initiated by the process



the molecules can be excited to high vibrational states (up to  $v=30$  for multilayer<sup>5</sup>  $^{13}\text{C}^{18}\text{O}$ ). In our previous experiments<sup>4,5</sup> we have suggested that up-pumping of CO in the monolayer can be driven by the excitation of multilayers. This is possible because the deficit energy  $\Delta E$  can be taken away quickly (in picoseconds<sup>15</sup>) by the lattice phonons of multilayers. This has been shown by others for solid  $\alpha$ -CO, with phonon frequencies near  $50 \text{ cm}^{-1}$ .<sup>15</sup> For the adsorbed monolayer, frustrated rotational motions against the surface have been reported to have a frequency of  $140 \text{ cm}^{-1}$  (Ref. 16) and would be too high to relieve the energy deficit. However, frustrated translational modes estimated to be less than  $50 \text{ cm}^{-1}$  (Refs. 16 and 17) may take up the excess energy, although possibly less efficiently.

Let us now summarize the origin of the overtone fluorescence. Laser excitation of low-lying vibrational levels is accompanied by up-pumping processes carrying the adsorbate to high- $v$  states. The fluorescence decay is a convolution of time constants of all the cascading molecules. The lifetime of 4.3 ms indicates that vibrational energy has been stored in a single layer of CO on NaCl(100) for milliseconds before it dissipates in any form. If the pumping is strong enough, population inversion can be achieved as demonstrated in the solid  $\alpha$ -CO system.<sup>4,5,15</sup> It appears that a monolayer of CO on NaCl(100) can be a unique lasing medium and would be a suitable candidate for constructing a laser with a single layer of oriented molecules.

The work presented here fills out our mapping of vi-

brational energy flow in the model system of CO on NaCl(100). We have now explored<sup>4</sup> all the possible relaxation channels of CO vibrational energy on the surface. A dephasing rate of  $k_{dp} \approx 10^{11} \text{ s}^{-1}$  has been estimated by temperature-dependent linewidth measurements.<sup>17</sup> From the fundamental infrared cross section the radiative rate constant of  $k_r^{1 \rightarrow 0} = 11 \text{ s}^{-1}$  was found.<sup>5</sup> An estimate of the surface relaxation rate  $k_{nr}$  can now be provided. Although the exact population distribution of the molecules in this experiment is not yet known, the distribution is expected to be much narrower and centered much lower than those in our multilayer experiments.<sup>5</sup> From  $v=1$  to  $v=15$  the radiative rate increases by a factor of 10.<sup>15</sup> We shall approximate the effective rate for all molecules populating this range of excited vibrational levels by taking a geometric mean. Scaling our measured value of  $k_r^{1 \rightarrow 0}$  by  $10^{1/2}$  we obtain  $k_r \approx 30 \text{ s}^{-1}$ . Therefore comparing the measured fluorescence rate of  $k_{obs} = \tau_{obs}^{-1} = 2.4 \times 10^2 \text{ s}^{-1} = k_r + k_{nr}$  with  $k_r$ , we find  $k_{nr} \approx 2 \times 10^2 \text{ s}^{-1}$ . This rate is 1 order of magnitude smaller than that previously reported.<sup>4,5</sup> The discrepancy is due in part to the difference in population distribution in these two experiments since, at higher vibrational states for the multilayer experiment (up to  $v=30$ ), the CO molecules relax faster and a larger relaxation rate results.<sup>5</sup> Another source for the disagreement may be in the approximations in the analysis required to extract a relaxation rate for the monolayer covered by overlayers which are also undergoing relaxation. Finally, we have directly measured the quantum yield of vibrationally induced desorption and found it to be inefficient when the molecules are populated at low vibrational states.<sup>6</sup> Using the estimate of  $k_{nr}$  and the analysis of our previous study,<sup>6</sup> the desorption rate,  $k_{vid} \leq 10^{-4} \text{ s}^{-1}$ , is orders of magnitude slower than the radiative rate.<sup>6</sup>

Absorbate-surface relaxation mechanisms are reviewed elsewhere.<sup>18-20</sup> For our system the theoretical interpretation of the surface relaxation rate has been established by a simple consideration of coupling between the CO oscillating dipole and surface phonons of NaCl(100).<sup>21</sup> Based on the dielectric properties of crystalline NaCl and the Co-(100)-surface separation, the theory predicts a rate-constant ratio of  $k_{nr}^{1 \rightarrow 0}/k_r^{1 \rightarrow 0} = 5$ ,<sup>6</sup> which is comparable with the ratio in the present study of  $k_{nr}/k_r \approx 7$ . Thus, while we monitor the population decay of CO vibrationally excited states through a  $\Delta v = -2$  overtone measurement, the primary relaxation channel is  $\Delta v = -1$  transfer to phonons of the substrate. The success of this classical treatment manifests the simplicity of the system of alkali halide surfaces. Excitation of the lattice vibration of the substrate is the principal relaxation channel, unlike the involved damping processes on metals.<sup>22</sup> The energy-transfer mechanisms can be further elucidated by applying the well-developed quantum-mechanical formalism,<sup>23</sup> which takes into account the coupling of surface-bond modes to our system when the detailed shape of the molecule-surface poten-

tial is accurately known. Our theoretical model to account for the exceedingly low vibrational desorption rate  $k_{\text{vid}}$  is given elsewhere.<sup>6</sup>

The relaxation of vibrationally excited CO on NaCl(100) on the millisecond time scale is in dramatic contrast to the relaxation of CO on Pt(111),<sup>2</sup> which is measured on the picosecond regime, or of H chemisorbed to Si(111),<sup>3</sup> which is on the nanosecond time scale. However, the absence of the electron-hole relaxation channel possible for metals, the weak coupling through a physisorbed bond, and the mismatch of the vibrational frequency ( $\approx 2000 \text{ cm}^{-1}$ ) with the surface phonon mode frequency ( $234 \text{ cm}^{-1}$ )<sup>24</sup> make NaCl(100) a uniquely passive substrate for CO.

To summarize, we have completed a map of vibrational energy flow on NaCl(100) by monitoring the infrared fluorescence from a monolayer of physisorbed CO. We have demonstrated in this paper that vibrational energy can be stored in adsorbates for more than milliseconds in surface systems whose substrate is remarkably passive to the molecular motions of interest. For the system of CO on NaCl(100), nearly 15% of the excited energy is released as infrared radiation. We believe that the study on alkali halide surfaces has led to a rich and interesting area that deserves more exploration.

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<sup>1</sup>A. L. Harris, L. Rothberg, L. H. Dubois, N. J. Levinos, and L. Dhar, Phys. Rev. Lett. **64**, 2086 (1990).

<sup>2</sup>J. D. Beckerle, M. P. Casassa, R. R. Cavanagh, E. J. Heilweil, and J. C. Stephenson, Phys. Rev. Lett. **64**, 2090 (1990).

<sup>3</sup>P. Guyot-Sionnest, P. Dumas, Y. J. Chabal, and G. S. Higashi, Phys. Rev. Lett. **64**, 2156 (1990).

<sup>4</sup>H.-C. Chang and G. Ewing, J. Vac. Sci. Technol. A **8**, 2644 (1990).

<sup>5</sup>H.-C. Chang and G. E. Ewing, J. Phys. Chem. (to be published).

<sup>6</sup>H.-C. Chang and G. E. Ewing, Chem. Phys. **139**, 55 (1989).

<sup>7</sup>S. Chiang, R. G. Tobin, P. L. Richards, and P. A. Thiel, Phys. Rev. Lett. **52**, 648 (1984).

<sup>8</sup>R. S. Disselkamp, H.-C. Chang, and G. E. Ewing, Surf. Sci. (to be published).

<sup>9</sup>C. Noda and G. E. Ewing, Surf. Sci. (to be published).

<sup>10</sup>H. H. Richardson, H.-C. Chang, C. Noda, and G. E. Ewing, Surf. Sci. **216**, 93 (1989).

<sup>11</sup>H.-C. Chang, H. H. Richardson, and G. E. Ewing, J. Chem. Phys. **89**, 7561 (1988).

<sup>12</sup>R. M. Dale, M. Herman, J. W. C. Johns, A. R. W. McKeller, S. Nagler, and I. K. M. Strathy, Can. J. Phys. **57**, 677 (1979).

<sup>13</sup>G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, 1950).

<sup>14</sup>N. Legay-Sommaire and F. Legay, Chem. Phys. **66**, 315 (1982).

<sup>15</sup>N. Legay-Sommaire and F. Legay, IEEE J. Quantum Electron. **16**, 308 (1980).

<sup>16</sup>H. H. Richardson, C. Baumann, and G. E. Ewing, Surf. Sci. **185**, 15 (1987).

<sup>17</sup>C. Noda, H. H. Richardson, and G. E. Ewing, J. Chem. Phys. **92**, 2099 (1990).

<sup>18</sup>Y. J. Chabal, Surf. Sci. Rep. **8**, 211 (1988).

<sup>19</sup>P. Avouris and B. N. J. Persson, J. Phys. Chem. **88**, 837 (1984).

<sup>20</sup>J. C. Tully, J. Electron Spectrosc. Relat. Phenom. **45**, 381 (1987).

<sup>21</sup>R. R. Chance, A. Prock, and R. Silbey, Adv. Chem. Phys. **37**, 1 (1978).

<sup>22</sup>B. N. J. Persson and M. Persson, Solid State Commun. **36**, 175 (1980).

<sup>23</sup>I. Benjamin and W. P. Reinhardt, J. Chem. Phys. **90**, 7535 (1989).

<sup>24</sup>J. J. Pireaux, P. A. Thiry, and R. Caudano, Surf. Sci. **162**, 132 (1985).