Vibrational Relaxation Lifetime of a Physisorbed Molecule at a Metal Surface

Sumit Kumar,[1,*] Hongyan Jiang,[1,†] Michael Schwarzer,[4] Alexander Kandratsenka,[1]
Dirk Schwarzer,[1] and Alec M. Wodtke [1,2,3]

[1]*Department of Dynamics at Surfaces, Max-Planck-Institute for Biophysical Chemistry, Am Fassberg 11, 37077 Göttingen, Germany*
[2]*Institute for Physical Chemistry, University of Göttingen, Tammannstrasse 6, 37077 Göttingen, Germany*
[3]*International Center for Advanced Studies of Energy Conversion, Georg-August University of Göttingen,
Tammannstrasse 6, 37077 Göttingen, Germany*
[4]*Institute of Aerodynamics and Flow technology, German Aerospace Center (DLR),
Bunsenstrasse 10, 37073 Göttingen, Germany*

Previous measurements of vibrational relaxation lifetimes for molecules adsorbed at metal surfaces yielded values of 1–3 ps; however, only chemisorbed molecules have been studied. We report the first measurements of the vibrational relaxation lifetime of a molecule physisorbed to a metal surface. For $CO(v = 1)$ adsorbed on Au(111) at 35 K the vibrational lifetime of the excited stretching mode is 49 ± 3 ps. The long lifetime seen here is likely to be a general feature of physisorption, which involves weaker electronic coupling between the adsorbate and the solid due to bonding at larger distances.

Introduction.—Vibrational excitation of gas-phase reactants can dramatically enhance reaction rates and control reaction pathways [1–3]. For chemical reactions on metal surfaces, vibrationally excited reactants are believed to thermalize with the solid much faster than dissociation, diffusion, and reaction. This is a central assumption of the Langmuir-Hinshelwood (LH) reaction mechanism [4–6], one of the foundations of heterogeneous catalysis. Nevertheless, some studies show that vibrationally excited molecules promote surface reactions even when the reaction is preceded by adsorption [7–9]. This raises the question: under what conditions is the thermalization assumption of the LH mechanism valid?

The rate of vibrational relaxation depends on the interactions of the molecule with the surface, which are thought to be well understood. When vibrationally excited CO is adsorbed on an insulator surface like NaCl, millisecond lifetimes are observed [10]; the vibrating CO molecules behave like classical oscillating dipoles, losing their energy to the NaCl lattice through the electromagnetic near field [11]. When $CO(v = 1)$ is chemisorbed on semiconductors like silicon, the lifetime is a few nanoseconds, reflecting the anharmonic coupling of the CO stretch to the phonon bath through the chemical bond made to the surface [12]. The shortest lifetimes observed are those of molecules chemisorbed to metals: 2.2 and 2.0 ± 1.0 ps for CO on Pt(111) [13] and Cu(100) [14], respectively. These short lifetimes result from Born-Oppenheimer breakdown, where vibrational energy is efficiently transferred to metal electronic excitation [15–28]. If this behavior was typical for adsorbates on metals, the thermalization assumption would be valid for LH reactions on a wide variety of important catalysts.

Physisorbed molecules interacting through dispersion forces with the metal are bound at longer distances and exhibit little or no electron exchange with the metal. Theory predicts physisorbed molecules exhibit longer vibrational relaxation lifetimes [29–33]. This has never been experimentally verified, as physisorbed molecules have very small spectroscopic transition strengths, making vibrational lifetime measurements difficult.

In this Letter, we report direct lifetime measurements for vibrationally excited molecules physisorbed to a metal surface. CO adsorbed on Au(111) exhibits an infrared CO-stretch frequency quite close to that of gas-phase CO. This, as well as its low desorption temperature (47 K), is a characteristic of physisorption. We use sum frequency generation detection to monitor the population of $CO(v = 1$ and $v = 0)$ after laser preparation of $CO(v = 1)$. Population in both states recovers with the same time constant, 49 ± 3 ps. This demonstrates that, when molecules interact with metal surfaces through dispersion forces, vibrational excitation can survive much longer than the typical times required for dissociation, diffusion, and reaction in surface chemistry. This suggests that physisorbed molecules may provide pathways for vibrationally promoted surface reactions, previously thought impossible.

Experimental.—We performed pump-probe experiments to derive the vibrational lifetime of $CO(v = 1)$ on a Au(111) surface at 35 K. Resonant pulsed infrared excitation was followed by a pair of laser pulses—a tunable IR pulse and a 532 nm up-conversion pulse—generating its frequency sum. The sum frequency generation (SFG) was enhanced when the IR pulse was resonant with CO vibration. All pulses were 20 ps in duration.
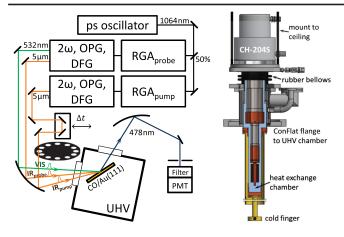
FIG. 1. Experimental setup to measure the vibrational lifetime of CO on Au(111) by surface pump-probe sum frequency generation. (Left) schematic diagram. (Right) Vibrational isolation for cryostatic cooling of the sample.

Figure 1 shows a schematic diagram of the experimental setup. Independently tunable IR pump and probe pulses were generated from two Nd:YAG-based 50 Hz regenerative amplifiers (RGA$_{pump}$ and RGA$_{probe}$) seeded with a common Nd:YAG-based ps oscillator. The RGA outputs excited two optical parametric generators (OPGs) and difference frequency generators (DFGs), providing pulse energies up to 300 μJ at wavelengths close to 5 μm and with a linewidth of 2 cm^{-1} (EKSPLA, PL2231-PG511-DFG). Typically, 30 and 9 μJ pulses were used for IR$_{pump}$ and IR$_{probe}$, respectively, and 10 μJ pulses of 532 nm light were used in the SFG detection. All three laser beams were p polarized and focused onto the CO/Au(111) surface at an incidence angle of ~80° from the surface normal using a 90°-off-axis parabolic mirror (25 cm effective focal length). The SFG signal at ~478 nm was collimated with a second parabolic mirror before it passed through an iris, a holographic notch filter centered at 532 nm, and a short wave pass filter (Semrock, 532 nm RazorEdge). The remaining light was detected with a photomultiplier (PMT, Hamamatsu 1P28). The pump-probe time delay was varied with a computer controlled translation stage. The pump-induced change of the SFG intensity was measured by blocking every second IR$_{pump}$ pulse with a synchronized chopper and averaging the signals with and without vibrational excitation of CO. Static SFG spectra were recorded as a function of the IR$_{probe}$ frequency with the pump pulse blocked.

Infrared reflection absorption (IRRA) spectroscopy was also performed using an IR femtosecond laser system providing pulses with a 200 cm^{-1} bandwidth at 5 μm (Coherent, Libra RGA, with home-built OPA and DFG). The laser beam was incident at the surface 86° from the surface normal with a polarization rotated 45° out of the incidence plane. The reflected light was resolved by a polarizer to give parallel (I_p) and perpendicular (I_s) intensities, whose spectra were independently measured

with a spectrometer employing a liquid-nitrogen cooled 2×32 array HgCdTe detector (Infrared Associates, Inc.). Since only p-polarized radiation can be absorbed by the adsorbate, the s component provides a pulse-to-pulse normalization reference to compensate laser intensity fluctuations. The reflectivity is calculated according to

$$R(\nu) = \left(\frac{I_p(\nu)}{I_s(\nu)}\right) / \left(\frac{I_p(\nu)}{I_s(\nu)}\right)_0, \qquad (1)$$

where the index 0 refers to a measurement from a clean Au(111) surface without CO.

The Au single crystal [MaTeck, diameter 1.0 cm, thickness 0.2 cm, orientation accuracy of (111) surface <0.1°, purity 99.999%] was enclosed in an ultrahigh vacuum (UHV) chamber and mounted to a sample holder of similar design as that described in Ref. [34]. The UHV chamber is equipped with two CaF$_2$ windows and pumped by a 550 l/s turbo pump (Leybold MAG W600iP), which is backed by a second 65 l/s turbo pump (Leybold Turbovac SL 80H) and an oil-based mechanical pump (Leybold Trivac D16B) providing a base pressure of $<1.5 \times 10^{-10}$ mbar. The Au crystal could be resistively heated (with a Heinzinger, PTN 32-20 power supply) or cooled to cryogenic temperatures using a closed cycle helium refrigerator (Janis research, CCS-XG-M/204N). The refrigerator was designed to reduce vibrations transferred from the cold head (SHI Sumitomo, model CH-204S) to the sample holder. The Joule-Thompson expander unit was mounted to the ceiling of the laboratory, while the sample mount was attached to the vacuum chamber that was mounted to the floor. A heat exchange chamber encapsulated by a rubber bellows filled with helium gas provided a thermal link between the expander and the sample mount. The Au crystal temperature was monitored with a type-E thermocouple inserted into a side hole of the crystal—the temperature was stabilized with a cryogenic temperature controller (Lakeshore, Model 336). The base temperature possible with this setup was 25 K.

Prior to every SFG experiment, the Au(111) surface was cleaned for 25 min with a 3 kV/10 μA argon ion sputtering beam (Specs Ar$^+$ gun, IQE 11/35). It was subsequently annealed at 1100 K for 30 min. Sample cleanliness was verified using an Auger spectrometer (Staib Instruments, ESA 100). The CO monolayer sample was characterized by temperature programmed desorption (TPD). The monolayer desorbs at 47 K in agreement with previous work [35,36]. Overlayers desorb at 30 K. For sample preparation and during the SFG experiment, the crystal was cooled to 35 K and dosed with a CO background pressure of 5×10^{-8} mbar, admitted to the chamber by a leak valve. Under these conditions, a full CO monolayer is formed since molecules desorbed by the laser pulses are readily replaced, but CO multilayers are not formed. IRRA experiments were performed on CO monolayers at 25 K with the leak valve closed. Here, the measurement times were short
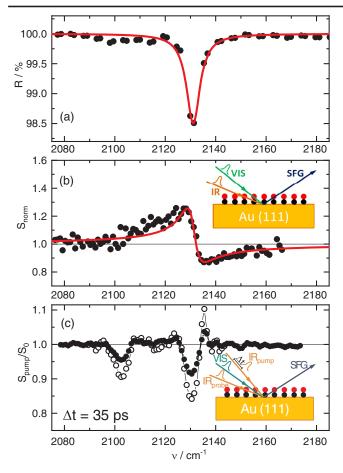
FIG. 2. (a) IRRA and (b) sum frequency generation spectra of monolayer CO on Au(111) at 25 K; the experimental data (full circles) of (a) and (b) were fitted with a Lorentzian line shape function and Eq. (2), respectively (red lines), using a common resonance frequency of $v_{01} = 2131$ cm^{-1} and a line width of $\Delta v_{01} = 6.5$ cm^{-1}. (c) The IR$_{pump}$-induced change in the SFG spectrum obtained 35 ps after exciting the sample with 30 μJ (full circles) and 60 μJ (open circles) pump pulses at 2131 cm^{-1} is shown ($T = 35$ K).

enough to ensure that multilayers did not form from residual CO, present in the chamber at a base pressure of $<10^{-10}$ mbar.

Results.—Static IRRA and SFG spectra of a monolayer of CO on Au(111) are shown in Figs. 2(a) and 2(b), respectively. The vibrational resonances at 2131 cm^{-1} are both assigned to the internal stretch fundamental of CO adsorbed on Au(111) terraces [37]. A small additional absorption between 2100 and 2115 cm^{-1} [Fig. 2(a)] arises from CO molecules bound at undercoordinated adsorption sites [35,37–39], which represent ∼1% of the surface area on our sample. The SFG spectrum exhibits a differential line shape arising from interference between the CO vibrational resonance and Au SFG 532 nm plasmon resonance. Because of the two contributions to the SFG signal and the fact that the IR$_{probe}$ laser power is wavelength dependent, the data of Fig. 2(b) were determined by

normalizing the spectrum obtained with a CO monolayer covering the surface (SFG$_{ML}$) to a separately measured SFG spectrum from bare Au(111) (SFG$_{Au}$). The ratio SFG$_{norm}$ = SFG$_{ML}$/SFG$_{Au}$ was then calculated and modeled using Eq. (2) [40]

$$I_{SFG} \propto |\chi_{Au}^{(2)} + \chi_{CO}^{(2)}|^2 = \left| \chi_{Au}^{(2)} + \frac{a_j}{(\omega_j - \omega - i\Gamma_j)} e^{-i\varphi_j} \right|^2,$$
(2)

where $\chi_{Au}^{(2)}$ and $\chi_{CO}^{(2)}$ are the Au and CO contribution to the surface's second-order susceptibility, respectively. The rhs of Eq. (2) is defined with a_j, ω_j, and Γ_j as oscillator strength, resonance frequency, and damping constant of the CO vibrational mode j, respectively. φ_j is the phase difference between the CO and the Au contributions—the phase of the latter is assumed to be constant over the frequency range of our spectra and arbitrarily set to zero.

The data of Fig. 2 were fitted with a Lorentzian line shape function for the IRRA spectrum [red line, Fig. 2(a)], and Eq. (2) for the SFG spectrum [red line, Fig. 2(b)], using global parameters for CO $v = 0 \rightarrow 1$ resonance frequency and line width: $\nu_{01} = \omega_{01}/(2\pi c) = 2131$ cm^{-1} and $\Delta\nu_{01} = \Gamma_{01}/(\pi c) = 6.5$ cm^{-1}. In addition, the fit to the SFG spectrum yields an amplitude ratio for CO to Au contribution: $a_{01}/|\chi_{Au}^{(2)}| = 0.19 \pm 0.02$ and the phase $\varphi_{01} = 14° \pm 4.0°$. The SFG spectrum also shows enhanced intensity between 2100 and 2115 cm^{-1}, indicating CO molecules adsorbed at defect sites of the surface [37].

Figure 2(c) shows changes in the SFG spectrum induced by a pump pulse resonant with the CO $v = 0 \rightarrow 1$ vibrational transition at 2131 cm^{-1} for a time delay between pump and probe $\Delta t = 35$ ps. While scanning the IR$_{probe}$ wave number, the SFG intensity was recorded with and without the IR$_{pump}$ pulse, yielding S_{pump} and S_0, respectively. S_{pump}/S_0 is plotted in Fig. 2(c) and shows pump-induced features at 2104, 2131, and 2135 cm^{-1}. We assign the feature at 2131 cm^{-1} to the depletion of the CO ground state vibrational population and the 2104 cm^{-1} feature to the increase in $v = 1$ population. The redshift of 27 cm^{-1} is consistent with the vibrational anharmonicity of CO [41]. We find that the ratio of intensities between the $0 \rightarrow 1$ and the $1 \rightarrow 2$ transitions is independent of pump pulse energy and that neither of the transitions is saturated. This linear dependence on population is a consequence of the fact that the SFG field from the CO sample is essentially heterodyne detected by interference with the much stronger SFG local oscillator field from the Au nonresonant background [42].

If the nonresonant background were much weaker than the resonant signal, the ν_{01} SFG intensity would be expected to be depleted after $0 \rightarrow 1$ pumping, whereas the ν_{12} signal would be enhanced [42]. Indeed this was seen for H/Si(111) [43,44]. Interestingly, Fig. 2(c) shows that
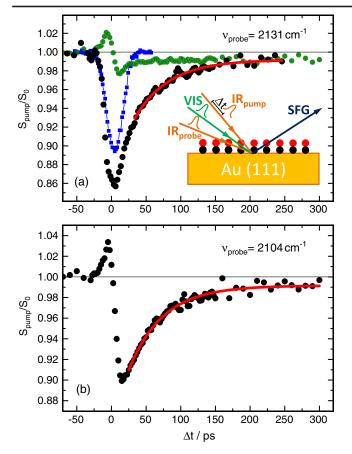
FIG. 3. Time-dependent SFG response of monolayer CO on Au(111) at 35 K with resonant excitation at $\nu_{pump} = 2131$ cm^{-1} and probing at (a) $\nu_{probe} = 2131$ cm^{-1} and (b) 2104 cm^{-1}, respectively (black points). Red lines are obtained from least-square fits, yielding a vibrational lifetime of $\tau = 49 \pm 3$ ps. (a) Green data points show the SFG response when the surface is excited off resonance from the CO $0 \to 1$ transition ($\nu_{pump} = 2112$ cm^{-1}). Blue squares represent the cross-correlation between the visible and IR pump pulse with a FWHM of 27 ps.

both signals move in the same direction. This can be rationalized if the phase for the $1 \to 2$ transition is $\varphi_{12} \sim 270°$ (recall $\varphi_{01} = 14°$; see above). This phase difference may be induced by a modification of the Au-CO interaction potential upon CO vibrational excitation, leading to a change in the Au-CO equilibrium distance.

For a heterodyne detected SFG signal, the pump-pulse-induced intensity changes for the $0 \to 1$ and the $1 \to 2$ transitions are expected to have the same amplitude. In Fig. 2(c), however, the $0 \to 1$ feature is clearly enhanced compared to the $1 \to 2$ feature. In the Supplemental Material [45] we show that this results from a combination of two effects on the $0 \to 1$ transition, an IR$_{pump}$-induced depletion of SFG intensity and a redshift of the excitonically coupled $0 \to 1$ band.

Figures 3(a) and 3(b) show the time dependence of these two signals after resonant excitation of the CO vibrational fundamental at 2131 cm^{-1} (black full circles). In both

cases, the pump-induced SFG displays a single exponential decay with time constant $\tau_1 = 49 \pm 3$ ps (red curves). The green circles in Fig. 3(a) show the SFG response when the pump laser is tuned off resonance, $\nu_{pump} = 2112$ cm^{-1}. We therefore assign the black data points of Figs. 3(a) and 3(b) to population relaxation from $v = 1$ to $v = 0$. To be precise, we measure the relaxation of exciton states of the adsorbed CO monolayer with dipole allowed transitions. As discussed in the Supplemental Material [45], these excitons arise from dipole-dipole coupling of the adsorbed CO molecules. The observation of a single exponential decay arising from a superposition of many dipole allowed transitions probing a manifold of exciton states indicates that these states are strongly coupled by dephasing with a characteristic time of ~1 ps (see Supplemental Material).

The lifetime observed in this Letter is much longer than seen in other related systems, where CO is chemisorbed to a metal. We next argue that the physisorption interaction between CO and Au(111) is responsible for the long lifetime.

Discussion.—There is strong evidence that CO is physisorbed on Au. The desorption temperature of CO from Au(111) is 47 K [35,36] and the activation energy of desorption is ~0.18 eV [56]. At low temperature, this activation energy is a good measure of the binding energy—the derived small binding energy is consistent CO being physisorbed to Au(111). In backbonding of chemisorbed species, metal electron density moves to the CO antibonding $2\pi^*$ orbital, simultaneously weakening the C—O bond while strengthening the C—metal bond. We probe the strength of backbonding in our samples by infrared spectroscopy. This shows that backbonding is absent in CO/Au, as the CO vibrational frequency ($\nu_{01} = 2131$ cm^{-1}) is quite close to that of gas-phase CO (2143 cm^{-1}), indicating little or no electron transfer to the $2\pi^*$ orbital of CO. Strong backbonding leads to strongly redshifted ν_{01} values: for example, 2103 cm^{-1} [57] and 2070 cm^{-1} [58] for CO chemisorbed on Pt(111) and Cu(111), respectively. Further evidence that CO is physisorbed to Au comes from density functional theory calculations that predict a binding energy of 0.1 eV [33], similar to the experimentally derived activation energy of desorption. Thus, all available evidence supports the conclusion that CO binds to Au(111) by dispersion forces.

There exists a strong theoretical foundation for the idea that a physisorbed molecule could have a much longer vibrational lifetime than its chemisorbed analogs. First, known mechanisms of vibrational relaxation are likely to shut down at the long binding distances typical of physisorbed molecules. For example, highly efficient vibrational relaxation can occur through electron transfer from the metal to the molecule forming a transient negative ion [15–21], a process which is strongly distance dependent due to image charge interaction. This is clearly described in Fig. 4 of Ref. [15] and Fig. 2 of Ref. [16]. In essence, the longer range repulsion associated with physisorption limits

image charge stabilization of the negative ion state, thus preventing electron transfer. When electron transfer is impossible, we may model the interactions between an oscillating dipole and a jellium electron gas [29–32] or by density functional perturbation theory following Fermi's golden rule expression for the nonadiabatic vibrational damping [33]. These methods predict vibrational relaxation lifetimes of CO on Au(111) between 250 ps [33] and 0.5–2 ns [29–32] (see Supplemental Material [45]). These theories support the idea that physisorbed molecules' vibrational lifetimes are long; however, they are not in agreement with the 49 ± 3 ps lifetime observed in this Letter at 35 K. Further theoretical work is required.

Thus, we conclude that physisorbed $CO(v = 1)$ may, by relaxing, still excite the metal's electron-hole pairs, but, due to its large distance to the metal, the strongest interactions are not possible. We emphasize that this explanation suggests there will be similar behavior for other physisorbed molecules.

Our measurements also shed light on recently reported molecular beam experiments [56], where $CO(v = 1 \text{ and } 2)$ was observed to desorb back to the gas phase after $CO(v = 2)$ adsorbed to Au(111). The degree of relaxation could not be quantified as the fraction of the CO sample desorbing, as $CO(v = 0)$ could not be measured. By assuming that the vibrational lifetime was comparable to thermal desorption lifetimes (100 ps), the order of magnitude of the vibrational lifetime could be estimated. This estimate suffered additional large uncertainties associated with the fact that the desorption rates used in the analysis were extrapolated from TPD measurements performed at much lower temperatures. The ambiguities and limitations inherent to this analysis are overcome in the present Letter, providing a quantitative measurement of the vibrational lifetime.

It is worth mentioning why similar results have not been obtained previously. Consider the magnitude of the infrared transition dipole moments for the internal stretching mode of a chemisorbed CO molecule that transfers electron density between the metal surface and the CO adsorbate during the course of CO vibration due to a backbonding interaction. This transition dipole moment is clearly much larger than that of an isolated CO gas-phase molecule, which a physisorbed CO more closely resembles. We carried out comparative measurements showing the peak infrared absorption cross section of CO on Au(111) is ~0.1 that of CO on Pt(111). In day-to-day operation, CO-SFG signals were far easier to find on Pt than on Au. It is not surprising then that no vibrational lifetimes of molecules physisorbed to a metal have been previously reported, since experiments with such species are inherently more difficult, in particular, for physisorbed CO with its low desorption temperature. More sensitive detection methods allowing additional measurements on systems like this would be of great value in establishing the generality of our findings.

———

*Present address: Department of Chemistry, Anugrah Memorial College, Gaya, Magadh University, Bodhgaya 824234, India.
†To whom all correspondence should be addressed. hongyan.jiang@mpibpc.mpg.de

[1] F. F. Crim, Science **249**, 1387 (1990).
[2] F. F. Crim, J. Phys. Chem. **100**, 12725 (1996).
[3] A. Sinha, M. C. Hsiao, and F. F. Crim, J. Chem. Phys. **94**, 4928 (1991).
[4] I. Langmuir, J. Am. Chem. Soc. **35**, 105 (1913).
[5] I. Langmuir, J. Am. Chem. Soc. **37**, 1139 (1915).
[6] C. N. Hinshelwood and C. R. Prichard, J. Chem. Soc. **127**, 327 (1925).
[7] A. V. Walker and D. A. King, J. Chem. Phys. **112**, 4739 (2000).
[8] D. C. Seets, M. C. Wheeler, and C. B. Mullins, Chem. Phys. Lett. **266**, 431 (1997).
[9] E. Dombrowski, E. Peterson, D. Del Sesto, and A. L. Utz, Catal. Today **244**, 10 (2015).
[10] H.-C. Chang and G. E. Ewing, Phys. Rev. Lett. **65**, 2125 (1990).
[11] L. Chen, J. A. Lau, D. Schwarzer, J. Meyer, V. B. Verma, and A. M. Wodtke, Science **363**, 158 (2019).
[12] K. Laß, X. Han, and E. Hasselbrink, J. Chem. Phys. **123**, 051102 (2005).
[13] J. Beckerle, R. R. Cavanagh, M. Casassa, E. J. Heilweil, and J. C. Stephenson, J. Chem. Phys. **95**, 5403 (1991).
[14] M. Morin, N. J. Levinos, and A. L. Harris, J. Chem. Phys. **96**, 3950 (1992).
[15] R. J. V. Wagner, N. Henning, B. C. Kruger, G. B. Park, J. Altschaffel, A. Kandratsenka, A. M. Wodtke, and T. Schafer, J. Phys. Chem. Lett. **8**, 4887 (2017).
[16] Y. H. Huang, C. T. Rettner, D. J. Auerbach, and A. M. Wodtke, Science **290**, 111 (2000).
[17] N. Shenvi, S. Roy, and J. C. Tully, Science **326**, 829 (2009).
[18] N. Bartels, K. Golibrzuch, C. Bartels, L. Chen, D. J. Auerbach, A. M. Wodtke, and T. Schafer, Proc. Natl. Acad. Sci. U.S.A. **110**, 17738 (2013).
[19] N. Bartels, B. C. Kruger, D. J. Auerbach, A. M. Wodtke, and T. Schafer, Angew. Chem., Int. Ed. Engl. **53**, 13690 (2014).
[20] J. W. Gadzuk, J. Chem. Phys. **79**, 6341 (1983).
[21] A. M. Wodtke, D. Matsiev, and D. J. Auerbach, Prog. Surf. Sci. **83**, 167 (2008).
[22] M. Head-Gordon and J. C. Tully, J. Chem. Phys. **103**, 10137 (1995).
[23] M. Head-Gordon and J. C. Tully, J. Chem. Phys. **96**, 3939 (1992).
[24] V. Krishna and J. C. Tully, J. Chem. Phys. **125**, 054706 (2006).
[25] J. W. Gadzuk and J. K. Norskov, J. Chem. Phys. **81**, 2828 (1984).
[26] K. Golibrzuch, N. Bartels, D. J. Auerbach, and A. M. Wodtke, Annu. Rev. Phys. Chem. **66**, 399 (2015).
[27] A. M. Wodtke, Chem. Soc. Rev. **45**, 3641 (2016).

[28] E. Hasselbrink, Curr. Opin. Solid State Mater. Sci. **10,** 192 (2006).

[29] B. Persson, J. Phys. C **11,** 4251 (1978).

[30] B. Persson and M. Persson, Surf. Sci. **97,** 609 (1980).

[31] B. N. J. Persson and S. Andersson, Phys. Rev. B **29,** 4382 (1984).

[32] A. Liebsch, Phys. Rev. Lett. **54,** 67 (1985).

[33] I. Loncaric, M. Alducin, J. I. Juaristi, and D. Novko, J. Phys. Chem. Lett. **10,** 1043 (2019).

[34] Q. Ran, D. Matsiev, A. M. Wodtke, and D. J. Auerbach, Rev. Sci. Instrum. **78,** 104104 (2007).

[35] J. M. Gottfried, K. J. Schmidt, S. L. M. Schroeder, and K. Christmann, Surf. Sci. **536,** 206 (2003).

[36] D. P. Engelhart, R. J. V. Wagner, A. Meling, A. M. Wodtke, and T. Schäfer, Surf. Sci. **650,** 11 (2016).

[37] J. Pischel and A. Pucci, J. Phys. Chem. C **119,** 18340 (2015).

[38] C. Ruggiero and P. Hollins, J. Chem. Soc., Faraday Trans. **92,** 4829 (1996).

[39] C. Ruggiero and P. Hollins, Surf. Sci. **377–379,** 583 (1997).

[40] Y. R. Shen, Proc. Natl. Acad. Sci. U.S.A. **93,** 12104 (1996).

[41] A. W. Mantz and J. P. Maillard, J. Mol. Spectrosc. **57,** 155 (1975).

[42] E. H. G. Backus, J. D. Cyran, M. Grechko, Y. Nagata, and M. Bonn, J. Phys. Chem. A **122,** 2401 (2018).

[43] C. Hess, M. Wolf, and M. Bonn, Phys. Rev. Lett. **85,** 4341 (2000).

[44] P. Guyot-Sionnest, Phys. Rev. Lett. **67,** 2323 (1991).

[45] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.123.156101 for (1) A model for excitonically coupled CO molecules in the monolayer. (2) An estimation of the vibrational lifetime based on theories by Persson and others, which includes Refs. [46–55].

[46] R. Disselkamp, H.-C. Chang, and G. E. Ewing, Surf. Sci. **240,** 193 (1990).

[47] D. J. Dai and G. E. Ewing, Surf. Sci. **312,** 239 (1994).

[48] S. Woutersen and P. Hamm, J. Phys. Condens. Matter **14,** R1035 (2002).

[49] A. S. Davydov, *Theory of Molecular Excitations* (Plenum, New York, 1971).

[50] P. Hamm, M. Lim, and R. M. Hochstrasser, J. Phys. Chem. B **102,** 6123 (1998).

[51] H.-J. Werner, Mol. Phys. **44,** 111 (1981).

[52] H.-J. Chen, J. Wu, H. Liu, and X.-L. Cheng, Chin. Phys. B **24,** 083102 (2015).

[53] M. Gajdoš, A. Eichler, and J. Hafner, J. Phys. Condens. Matter **16,** 1141 (2004).

[54] C. Kittel, *Introduction to Solid State Physics*, 8th ed. (Wiley, New York, 2005).

[55] R. J. Maurer, M. Askerka, V. S. Batista, and J. C. Tully, Phys. Rev. B **94,** 115432 (2016).

[56] P. R. Shirhatti, I. Rahinov, K. Golibrzuch, J. Werdecker, J. Geweke, J. Altschäffel, S. Kumar, D. J. Auerbach, C. Bartels, and A. M. Wodtke, Nat. Chem. **10,** 592 (2018).

[57] J. V. Nekrylova, C. French, A. N. Artsyukhovich, V. A. Ukraintsev, and I. Harrison, Surf. Sci. Lett. **295,** L987 (1993).

[58] B. E. Hayden, K. Kretzschmar, and A. M. Bradshaw, Surf. Sci. **155,** 553 (1985).