

Direct Observation of Vibrational Energy Delocalization on Surfaces: CO on Ru(001)

Ch. Hess and M. Wolf

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, 14195 Berlin, Germany

M. Bonn

Leiden Institute of Chemistry, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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We report the experimental observation of the gradual transition from a local oscillator to a two-dimensional delocalized phonon, observed for the CO-stretch vibration of carbon monoxide adsorbed on a Ru(001) surface by means of broadband-infrared saturation sum-frequency spectroscopy. The data are theoretically reproduced by an exchange model with residence times of the excitation down to 2.5 ps.

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The nature of elementary excitations—especially its localized or delocalized character—is of general importance in physics, chemistry, and biology: Delocalization, for example, plays a key role in the process of energy migration of electronic excitations in the photosynthetic unit [1]. Localization of vibrational energy in a specific bond is essential to achieve mode-selective chemistry [2]. On surfaces, multivibrational excitation and bond breaking [3] requires that the lateral spreading of vibrational energy through intermolecular coupling is weak. Because of its relevance, the localized or delocalized nature of vibrational excitations on surfaces has been the subject of extensive study, both with conventional (see, e.g., [4,5]) and time-resolved [6–11] infrared spectroscopy. However, the transition from a local oscillator to a delocalized phonon with the onset of intermolecular interactions has remained largely unexplored. In this Letter, we report the direct observation of the transition from a localized to a delocalized surface vibration through nonlinear surface spectroscopy and obtain novel information on the dynamics of energy delocalization in the adlayer.

Molecules interacting through their dipolar fields can exchange vibrational energy. As a result, for strongly interacting molecules on surfaces, vibrational energy can be delocalized over several bonds or even the whole adlayer. The transition from a well-localized to a delocalized excitation, the phonon-localization transition, has been described theoretically in great detail [12] and has been observed in three-dimensional molecular solids with linear spectroscopic techniques [13,14]. On surfaces, information on vibrational energy delocalization has been obtained through the infrared line shape of CO on Ru(001) [5] in conjunction with theoretical modeling of the coverage-dependent dipole coupling [15].

In the novel approach presented here, the $^{12}\text{C}^{16}\text{O}$ -stretch vibration of CO adsorbed on Ru(001) is strongly excited by an ultrashort infrared laser pulse, so that a significant amount of the CO molecules is pumped from the ground ($\nu = 0$) to the first vibrationally excited ($\nu = 1$) state. For the time that the molecules remain excited, absorption from ($\nu = 1$) to ($\nu = 2$) can occur,

giving rise to the so-called “hot band.” The hot-band transition ($\nu = 1 \rightarrow 2$) is shifted from the fundamental ($\nu = 0 \rightarrow 1$) by twice the vibrational anharmonicity Γ [$\Gamma = (\nu_{01} - \nu_{12})/2$]. The strength of the intermolecular interaction, defined by the dispersion of the vibrational mode W [12], can be tuned by simply changing the surface coverage [in our experiment from 0.006 monolayers (ML) to 0.33 ML]. For $W \geq \Gamma$, the vibration will become delocalized, giving rise to a profoundly different behavior of the ($\nu = 1$) state, accompanied by dramatic changes in the hot-band transition. This method allows us to directly observe the transition in two dimensions and determine energy delocalization times, typically picoseconds. It should be noted that the technique and theoretical approach presented here apply in general to systems of arbitrary dimensionality.

The experiments were performed with a femtosecond laser system delivering tunable (2–10 μm) IR pulses with a bandwidth of about 100 cm^{-1} (FWHM) and a pulse energy of up to 11 μJ (beam waist at focus: 0.3 mm FWHM). The center frequency of the IR pulses is resonant with the C-O vibration. The signal is generated by mixing the IR pulse on the surface with a narrow-bandwidth ($\sim 4 \text{ cm}^{-1}$) visible (VIS, 4 μJ , 800 nm) pulse, as shown schematically in the inset in Fig. 1. Sum-frequency generation (SFG) is a second-order nonlinear optical process in which two incident waves at ω_{VIS} and ω_{IR} generate an output at $\omega_{\text{SFG}} = \omega_{\text{VIS}} + \omega_{\text{IR}}$, where energy and momentum must be conserved [16]. When using broadband-IR pulses, resonant enhancement will occur only for frequencies ω_{IR} which are resonant with the vibrational transition. Thus, vibrational spectra can be obtained without scanning the IR frequency [17,18]. The SFG beam is focused into a spectrograph and dispersed across an intensified charge-coupled device detector. The Ru(001) sample was mounted in a UHV chamber (base pressure 1×10^{-10} mbar) and could be cooled to 95 K. CO exposure was performed via a pinhole doser or a variable leak valve. For all coverages reported here, CO is adsorbed on a-top Ru sites [19]. Transient surface temperature increases due to nonresonant laser heating are

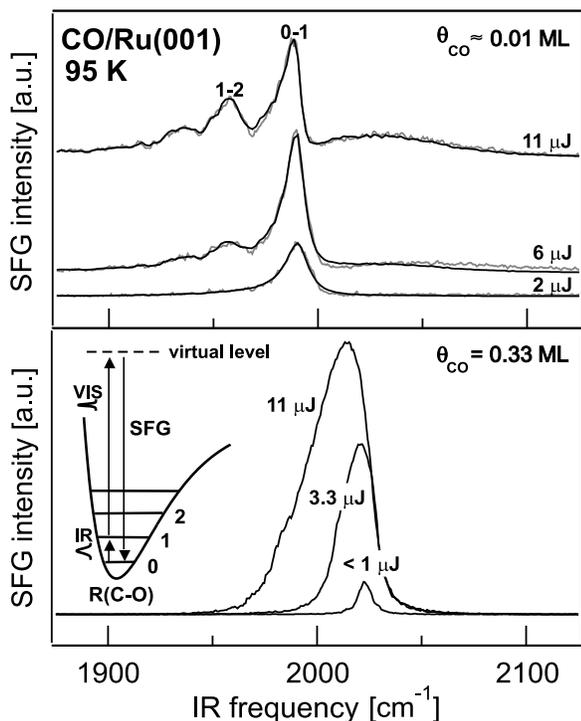


FIG. 1. Upper panel: SFG spectra (gray lines) together with the least-squares fits to the data (black lines) for a CO coverage of about 0.01 ML. At 11 μJ the $\nu = 1 \rightarrow 2$ and the $\nu = 2 \rightarrow 3$ hot band of the CO-stretch vibration can be seen besides the fundamental. IR energies can be converted to fluences (in mJ/cm^2) by multiplication with 1.4. Lower panel: SFG spectra of the CO-stretch vibration of $(\sqrt{3} \times \sqrt{3})\text{-CO}/\text{Ru}(001)$ ($\theta = 0.33$ ML) as a function of IR energy at 95 K. The inset shows the principle of IR-VIS SFG (see text). The difference in resonance frequency of the fundamental for the two coverages at low excitation is due to the effect of intermolecular coupling [5].

below 30 K and are therefore unimportant in the interpretation of the data. An extensive description of the complete experimental setup and surface cleaning procedures can be found in [20].

For the experiments performed here, the IR pulse creates not only the SFG signal but also saturates the fundamental transition ($\nu = 0 \rightarrow 1$), so that an additional SFG signal originating from the $\nu = 1 \rightarrow 2$ hot-band transition is produced which results from a fourth-order ($\chi^{(4)}$) nonlinear optical process. This is demonstrated in the upper panel in Fig. 1 where data for low CO coverage of about 0.01 ML are depicted [21]: With increasing IR power the $\nu = 1 \rightarrow 2$ hot band of the CO-stretch vibration becomes clearly visible at $1961.4 \pm 0.3 \text{ cm}^{-1}$, in addition to the fundamental transition at $1990.4 \pm 0.1 \text{ cm}^{-1}$ which is also observed at lower IR energies. Evidently, a significant fraction of the CO oscillators is excited to the first vibrational state. The third resonance around 1938 cm^{-1} arises from two contributions: the $\nu = 2 \rightarrow 3$ hot band and the fundamental transition of the natural abundant $^{13}\text{C}^{16}\text{O}$ in $^{12}\text{C}^{16}\text{O}$ gas. The SFG spectra $I_{\text{SFG}}(\omega)$ can be reproduced very well by an expression for the second-order nonlinear

susceptibility consisting of a nonresonant term $\chi_{\text{NR}}^{(2)}$ arising from the surface region of the metal and a resonant term $\chi_{\text{R}}^{(2)}$ associated with the vibrational transition [22,23]:

$$I_{\text{SFG}}(\omega) = |\chi^{(2)}|^2; \quad \chi^{(2)} = \chi_{\text{NR}}^{(2)} + \chi_{\text{R}}^{(2)} = A_0 e^{i\phi} + \sum_n \frac{A_n}{\omega_{\text{IR}} - \omega_n + i\Gamma_n}, \quad (1)$$

where the vibrational resonances are described by their resonance frequencies ω_n , linewidths $2\Gamma_n$, and amplitudes A_n so that the $\chi^{(4)}$ contribution is incorporated in $\chi^{(2)}$. A_0 is the amplitude of the nonresonant susceptibility and ϕ is its phase relative to the vibrational resonance.

At the low coverage of 0.01 ML, the distance between the CO molecules is sufficiently large so that interaction between CO molecules is small. Thus, the CO molecules exhibit local-oscillator behavior, and the system can be fully characterized by the anharmonicity of the CO-stretch vibration: An anharmonicity of $\Gamma = (\nu_{01} - \nu_{12})/2 = 13.6 \text{ cm}^{-1}$ [23] is obtained in very good agreement with results from overtone spectroscopy [24].

At much higher coverages strikingly different SFG spectra are obtained: For 0.33 ML, no hot band is observed, but as shown in the lower part of Fig. 1, increasing IR power leads to a broadening and a redshift of the resonance as a result of saturation. The excited-state spectra show a single broadened feature with a non-Lorentzian line shape and an asymmetric tail to the long-wavelength side. These observations can be explained only by taking into account CO-CO interactions in addition to the anharmonicity of individual CO molecules. At 0.33 ML dipole-dipole coupling between the adsorbed molecules leads to a delocalization of vibrational energy within the CO adlayer. Following Shen *et al.* [12] the intermolecular interaction of a vibrationally excited layer can be calculated by perturbation theory using a mean-field approximation: In the limit $\Gamma < W$ the peak of the optical absorption for a system with C phonons excited per CO oscillator occurs at $\omega = \omega_0 - 4C\Gamma$. With $\Gamma = 13.6 \text{ cm}^{-1}$ (see above), the frequency shift of $\omega - \omega_0 = -9 \text{ cm}^{-1}$ at the highest degree of excitation leads to a value of $C \approx 0.17$ for the number of excited phonons per CO molecule. Thus, increasing saturation of the fundamental transition leads to a continuous shift of the absorption spectrum to the long-wavelength side as a result of increasing excited state population C . Unfortunately, this theory does not contain a quantitative expression for the spectral changes accompanying the phonon-localization transition. We present one below.

Figure 2 depicts the measurements of the phonon-localization transition (left panel), along with calculations that fully reproduce the spectra (right panel). The experimental SFG spectra of CO adsorbed on Ru(001) were recorded at a temperature of 95 K for increasing

CO coverage [25] (viz. increasingly strong intermolecular coupling). With increasing coverage the $\nu = 1 \rightarrow 2$ hot band *gradually* disappears, indicating a transition from discrete vibrational energy levels to a continuum of states: the delocalization of vibrational energy. Its gradual character demonstrates that the phonon-localization transition is a soft transition in the character of the excitation, which seems to be complete at a CO coverage as low as 0.025 ML, where the hot band is no longer discernible. The continuous character of the transition is in agreement

with theoretical predictions [12] and previous observations in three-dimensional systems [13,14].

The calculated spectra in the right panel of Fig. 2 result from a model which describes the energy delocalization as a function of finite residence time of the ($\nu = 1 \rightarrow 2$) excitation on one oscillator, before hopping to a neighboring oscillator. To this end, we have modified the exchange model by Shelby *et al.* [26], which was successfully employed to describe line shapes in the condensed phase. The overall spectrum reads [27]

$$I(\omega) = \frac{\gamma_{\text{hop}} n_{\text{exc}} (2\Gamma)^2 / (1 + n_{\text{exc}})}{[\omega'^2 - \Gamma^2]^2 + [\gamma_{\text{hop}}(\omega' + \Gamma) + \gamma_{\text{hop}} n_{\text{exc}}(\omega' - \Gamma)]^2},$$

where $\omega' = \omega - \omega_0 - \Gamma$ (with ω_0 the fundamental transition), γ_{hop}^{-1} is the average time an oscillator retains the excited state frequency, before the excitation hops to another oscillator, $n_{\text{exc}}/(n_{\text{exc}} + 1)$ is the fraction of excited CO molecules, and Γ is the anharmonicity [27]. Lifetime broadening along with the instrumental response function is included by convoluting the resulting spectra with a 7 cm^{-1} Lorentzian. Since Γ and n_{exc} can be obtained directly from low-coverage data of the left panel, the only adjustable parameter in the model is the excitation residence time γ_{hop}^{-1} . With increasing coverage the intermolecular coupling increases and therefore the excitation residence time decreases. This model describes the effect of vibrational energy delocalization on the line shape of the fundamental and the hot-band transition in a phenomenological manner, where the strength of the dipole coupling determines the rate of exchange, and is independent of the dimensionality of the system. As can be seen from Fig. 2, the model describes the data remarkably well: Both the gradual filling of the gap between the two transitions as well as the redshift of the resonance frequency of the fundamental transition as a result of increasing energy exchange are reproduced by varying γ_{hop} between 0 and 2.5 ps^{-1} . This

value can be compared with the ($\nu = 1$) vibrational energy relaxation time (T_1) of $\sim 2 \text{ ps}$ for CO on Pt(111) [7] and Cu(100) [28] with energy transfer to the substrate through electron-hole pair excitation. Surprisingly, the time scales for the vibrational energy decay into the substrate and the intermolecular energy transfer are very similar. This demonstrates the importance of intermolecular vibrational energy delocalization in competition with other energy relaxation processes on surfaces.

To gain insight into the mechanisms leading to the intermolecular energy exchange, it is helpful to consider the coverage in terms of intermolecular distances. For 0.017 ML an excitation residence time of 6 ps is observed. At this coverage the average distance between adsorbed molecules amounts to 3.5–4 lattice units (approximately 10 \AA) [29]. This distance is too large for direct overlap of wave functions to occur, so that the energy exchange must be explained by dipole-dipole coupling.

A useful measure of the strength of the dipole-dipole coupling is the dispersion caused by this intermolecular interaction [30]. From the experimental data of Fig. 2 the dispersion for CO/Ru(001) can be extracted at very low coverages: Figure 3 depicts the two-phonon bound state (TPBS) shift, defined as the difference in frequency between the $\nu = 0 \rightarrow 1$ and $\nu = 1 \rightarrow 2$ transition, as a function of coverage. The transition frequencies are derived from the least-squares fits to experimental data taken at low IR energies ($3\text{--}6 \mu\text{J}$) in order to minimize the effect of saturation. Together with the data the prediction from a model by Kimball, Fong and Shen (KFS model) [12] assuming a system of coupled anharmonic oscillators with anharmonicity Γ and dispersion W is shown. For Γ the experimentally determined value of 13.6 cm^{-1} (see above) is taken. W is treated as a free parameter assuming a linear increase as a function of CO coverage. Although Ref. [12] does not provide an explicit expression for a 2D system, the expressions for a one-dimensional linear chain and a 3D lattice with a semicircular density of states results in very similar dispersions: To obtain the best agreement between experiment and theory W has to increase by $424 \text{ cm}^{-1}/\text{ML}$ and $405 \text{ cm}^{-1}/\text{ML}$ at these low coverages, for the 3D and the 1D model,

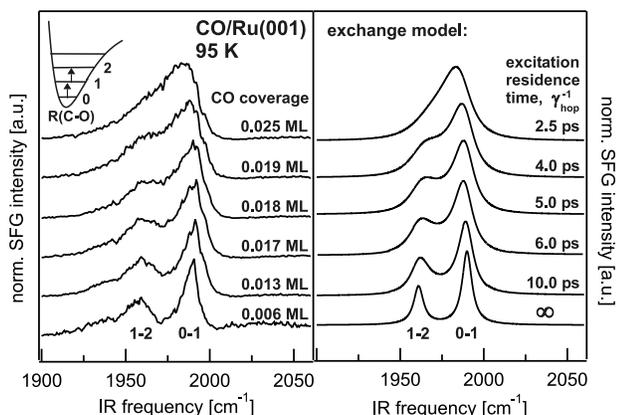


FIG. 2. Left panel: SFG spectra of the CO stretch as a function of CO coverage at 95 K. With increasing coverage the $\nu = 1 \rightarrow 2$ hot band decreases and disappears at a coverage of 0.025 ML. Right panel: Prediction of the exchange model for varying excitation residence times.

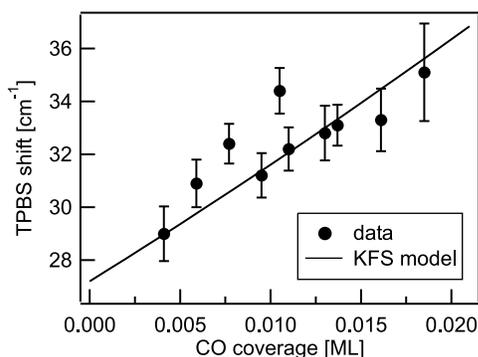


FIG. 3. Difference in frequency between the $\nu = 0 \rightarrow 1$ and $\nu = 1 \rightarrow 2$ transitions (TPBS shift) as a function of CO coverage together with the prediction from the three-dimensional KFS model for an increase in dispersion width W of $424 \text{ cm}^{-1}/\text{ML}$. To minimize the effect of saturation IR energies of $3\text{--}6 \mu\text{J}$ have been used.

respectively. These values are very satisfactory, since it means that at 0.025 ML coverage where the phonon-localization transition occurs (which is theoretically predicted to take place when $\Gamma = W$), the dispersion amounts to roughly $(0.025 \times 410) \text{ cm}^{-1} = 10.3 \text{ cm}^{-1}$, which is very close to the anharmonicity of 13.6 cm^{-1} .

To summarize, femtosecond vibrational saturation spectroscopy of the CO-stretch vibration of CO/Ru(001) allows the transition from localized oscillators to delocalized phonons to be observed directly by changing the CO coverage. Thereby, the $\nu = 1 \rightarrow 2$ hot-band transition of the CO-stretch vibration serves as a sensitive indicator for vibrational energy localization. With increasing coverage the lateral interactions between the adsorbed molecules and therefore the delocalization of vibrational energy increases which leads to the disappearance of the hot band at a coverage around 0.025 ML . In conjunction with a modified exchange model, the dynamics of the delocalization process can be deduced, and the excitation is found to “hop around” on time scales down to 2.5 ps , decreasing with increasing coverage. These experiments open the way to understand the competition between intramolecular and intermolecular energy relaxation on surfaces which is essential to bond-selective chemistry on surfaces.

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