

Dynamics of the C-O Stretch Overtone Vibration of CO/Ru(001)

P. Jakob

Physik-Department E 20, Technische Universität München, D-85747 Garching, Germany

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The vibrational spectra of CO adsorbed on Ru(001) have been reinvestigated by infrared absorption spectroscopy at considerably improved sensitivity. A localized two-phonon bound state of the internal stretching mode has been identified. The anharmonicities of the adsorbate vibration have been determined and found to be 18.5 cm^{-1} for $^{12}\text{C}^{16}\text{O}$ and about 17.7 cm^{-1} for $^{12}\text{C}^{18}\text{O}$ and $^{13}\text{C}^{16}\text{O}$, which is about 40% higher than found for the gas phase species. Rapid broadening of the overtone band with increasing temperature is attributed to the thermally activated decay of the two-phonon bound state into single phonon states. [S0031-9007(96)01523-2]

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Vibrational overtone spectra provide extremely important information on the shape of the potential curves and the dissociation energies of individual molecules. So far, very little attention has been devoted to this subject in the vibrational spectroscopy of adsorbate species, mostly because of severe sensitivity problems. These limitations usually do not apply to studies of macroscopic solids and gaseous samples for which extensive data have been accumulated in the past. Adsorbate species in the (sub) monolayer regime, however, experience extra chemical interaction with the (metal) substrate which modify their electronic properties and the potential energy curves which set the internal vibrational frequencies. In addition, new molecule-substrate vibrations are created (hindered translations and rotations). Vibrational spectra are usually interpreted within the harmonic approximation and assuming a linear dependence of the dipole moment μ on the vibrational coordinate q_i , which implies a strict $\Delta v = \pm 1$ selection rule in photon absorption and equidistant energy levels (for an overview on vibrational spectroscopy of adsorbates, see Ref. [1]). The vibrational wave functions are orthogonal and no interaction among them is possible. However, energy and phase relaxation phenomena [2,3] indicate that deviations from this idealized situation occur. First, anharmonic corrections of the vibrational potential proportional to q_i^3 and q_i^4 lead to corrections of the energy levels

$$E_v = \hbar\omega_e\left(v + \frac{1}{2}\right) - \hbar\omega_e x_e\left(v + \frac{1}{2}\right)^2 + \hbar\omega_e y_e\left(v + \frac{1}{2}\right)^3 + \dots$$

which cause them to converge at higher v . Here v is the vibrational quantum number, ω_e the vibrational frequency in the harmonic approximation, x_e and y_e the lowest level anharmonic corrections to ω_e . The $\Delta v = \pm 1$ selection rule then is weakened as the vibrational wave functions $|\Psi_{\text{vib}}\rangle$ can no longer be described by Hermite polynomials. Transitions between the ground state and E_1 or E_2 (in units of cm^{-1}) are expected at $\nu'_{\text{C-O}} = \hbar\omega_e - 2\hbar\omega_e x_e$ and $\nu''_{\text{C-O}} = 2\hbar\omega_e -$

$6\hbar\omega_e x_e = 2\nu'_{\text{C-O}} - 2\hbar\omega_e x_e$, respectively, for our case of CO adsorbed on Ru(001). Second, higher order terms of the dipole moment

$$\mu = \mu_0 + \sum_i \frac{\partial\mu}{\partial q_i} \Delta q_i + \sum_{ij} \frac{\partial^2\mu}{\partial q_i \partial q_j} \Delta q_i \Delta q_j + \dots$$

cause $\Delta v = \pm 2, 3, \dots$ transitions to occur even for harmonic potentials. Nondiagonal terms $\frac{\partial^2\mu}{\partial q_i \partial q_j} \Delta q_i \Delta q_j + \dots$ with $i \neq j$ produce combination bands with $\Delta v_i = \pm 1$ and $\Delta v_j = \pm 1$ selection rules [4].

The detection of such overtone and combination bands is difficult as the corrections to the harmonic approximation and higher order terms of μ are small at low v . Only recently has it been possible to study such higher order transitions of adsorbates by the infrared absorption technique [5]. Earlier results obtained by high resolution electron energy loss spectroscopy (HREELS) were limited by the instrumental resolution, and useful parameters on the shape of the vibrational potential could not be obtained [6]. In many cases overtone intensities are enhanced by Fermi resonances which eases their detection considerably, but the correlated extra line shift renders their spectral position somewhat uncertain [7]. There are several examples of two-phonon bound states of adsorbates with two vibrational quanta being localized at a single oscillator. The most elaborate overtone studies of adsorbate species so far have been obtained by the nonlinear sum frequency generation technique (SFG) for hydrogen adsorbed on various silicon and diamond surfaces [H/Si(111), H/Si(100), and H/C(111)] [8]. Two-phonon bound states (localized overtone bands) could be detected in each of these cases by employing a two color pump/probe SFG setup.

However, even the most recent data [5,8] preclude an accurate determination of the anharmonicity constants as the linewidths of the overtone or combination bands are broad, the signal/noise ratio poor, and the positions of the (nondipole shifted) vibrational frequencies of the localized component fundamental modes not known precisely. In this Letter we report a detailed investigation of infrared absorption spectra of the $\nu''_{\text{C-O}}$ -overtone of

$(\sqrt{3} \times \sqrt{3})\text{CO}/\text{Ru}(001)$. This system was chosen because of the high homogeneity to which the layer can be prepared. From an analysis of the temperature dependency of the line positions and widths, the thermally activated decay of a two-phonon bound state into two single phonon states could be investigated. The existence of naturally abundant $^{13}\text{C}^{16}\text{O}$ enabled the exact line position of the noncoupled (singleton) $^{12}\text{C}^{16}\text{O}$ stretching mode to be derived, which allowed the first accurate determinations of the anharmonicity constants of adsorbate vibrations to be made. Our observations are assisted by isotopic substitution experiments ($^{12}\text{C}^{16}\text{O} \leftrightarrow ^{12}\text{C}^{18}\text{O} \leftrightarrow ^{13}\text{C}^{16}\text{O}$) which display similar line shifts and line broadenings. In contrast to using HREELS or SFG, the direct excitation of $\nu = 2$ states by the absorption of infrared photons avoids ambiguities arising from multiple energy losses and transient bleaching of the vibrational levels involved. The extraction of the anharmonicity parameters and the spectral line shapes is further aided by the high intrinsic resolution of infrared absorption spectroscopy (IRAS).

The experiments were performed in a specially designed ultrahigh vacuum chamber (base pressure 7×10^{-11} mbar) with standard sample cleaning and characterization facilities. The Michelson interferometer is a highly stable evacuable Bruker 66V bench and the infrared absorption spectra were obtained using an MCT detector with a low frequency cutoff at 600 cm^{-1} . Typically 2000 scans at 2 cm^{-1} resolution were coadded (corresponding to a total accumulation time of 540 s each for the reference and the sample spectrum) to obtain reproducibilities of 1 part in 15 000 in the region of the $\nu''_{\text{C-O}}$ overtone. The Ru(001) sample was oriented within $\pm 0.1^\circ$ and surface cleanliness was checked by standard procedures [9]. The sample could be cooled to 30 K and heated resistively. Gas exposure was performed via a microcapillary array at the IRAS measurement position.

In Fig. 1 spectra of the fundamental $\nu'_{\text{C-O}}$ -mode as well as the accompanying mode of naturally abundant $^{13}\text{C}^{16}\text{O}$ and the first overtone $\nu''_{\text{C-O}}$ [Fig. 1(b)] are displayed for the $(\sqrt{3} \times \sqrt{3})\text{CO}/\text{Ru}(001)$ layer using a spectral resolution of 2 cm^{-1} . The $\nu'_{\text{C-O}}$ peak absorption and linewidth at 30 K are 14.5% and 4.3 cm^{-1} , respectively, leading to an integrated absorbance of 0.45 cm^{-1} . This value agrees approximately with the numbers reported in the literature for similar setups (incidence angle 84°) [10]. It is apparent from our measured 4.3 cm^{-1} linewidth that layer inhomogeneity and surface defect density are extremely low. The measured width of 6.5 cm^{-1} of the overtone band at 30 K demonstrates that at low temperatures this mode displays a quite narrow line shape as well.

For a proper evaluation of the vibrational anharmonicities associated with a two-phonon bound state the line position of the *localized* fundamental mode $\nu'_{\text{C-O,loc}}$ is needed, i.e., disregarding any frequency shifts related to dynamic dipole coupling which are responsible

for the delocalized nature of the strong fundamental $\nu'_{\text{C-O}}$ mode. In the case of adsorbed CO on Ru(001) this dynamic (blue-) shift amounts to 42.2 cm^{-1} at 0.33 ML. This intermolecular coupling mechanism also causes a *red shift* of the minority $^{13}\text{C}^{16}\text{O}$ internal stretch mode by 2.5 cm^{-1} for the layer in Fig. 1. Further taking into account the $\nu'_{\text{C-O}}$ isotopic shift when exchanging regular CO with $^{13}\text{C}^{16}\text{O}$ [$\Delta\omega = -45.1 \text{ cm}^{-1}$; this value has been determined experimentally for a strongly diluted layer of mixed CO isotopes adsorbed on Ru(001)] the line position of the localized (singleton) $^{12}\text{C}^{16}\text{O}$ species can be determined (1988.6 cm^{-1} at 30 K). The anharmonicity $\hbar\omega_e x_e$ of the internal stretch mode of CO/Ru(001) is then easily calculated to be 18.5 cm^{-1} for $^{12}\text{C}^{16}\text{O}$, which is considerably larger than the value for gas phase CO (13.29 cm^{-1}) [11]. This indicates that despite the close proximity of the vibrational frequencies of gas phase CO and adsorbed CO/Ru(001) the vibrational potential and, as a consequence, the electronic structure looks very different. The validity of these findings has been verified by equivalent studies of layers containing $^{13}\text{C}^{16}\text{O}$ or $^{12}\text{C}^{18}\text{O}$ at 0.33 ML. A summary of the respective line positions is given in Table I. Note that the $\nu_{\text{C-O}}$ anharmonicities of these isotopically labeled CO species are lower than the corresponding value of $^{12}\text{C}^{16}\text{O}$ because of their lower vibrational frequencies. Assuming a Morse potential for the internal CO bond the related dissociation energy $E_D = \frac{\hbar\omega_e}{4x_e}$ can be approximately determined using these parameters. $6.85 \pm 0.05 \text{ eV}$ is obtained for all three CO isotopic species which is clearly lower than the 10.97 eV derived from the anharmonicity of gas-phase CO (experimental value $E_D(\text{CO} - \text{gas}) = 11.09 \text{ eV}$ [11]).

We now will turn to the details of the temperature dependence of line positions and widths. Both quantities are plotted in Figs. 2 and 3 versus temperature. The $\nu''_{\text{C-O}}$ overtone frequency displays a considerably smaller red shift compared to the fundamental (delocalized) $\nu'_{\text{C-O}}$ mode [for this comparison $1/2 \times \Delta\nu'_{\text{C-O}}(T)$ is considered] and it closely follows $\nu'_{\text{C-O}}$ of the localized $^{13}\text{C}^{16}\text{O}$ species; the temperature dependence of the linewidths of all three bands differ strikingly; the localized modes broaden substantially faster and, in particular, $\nu''_{\text{C-O}}$ reaches an impressive value of 30 cm^{-1} even at 200 K from 6 cm^{-1} at 30 K. Vibrational energy damping via electron-hole pair creation appears rather unlikely in view of the temperature interval being so small compared to the vibrational energy. Also such an effect should show up similarly for the fundamental modes as well. The contribution of a dephasing process to the linewidth can be estimated by comparison to the localized $^{13}\text{C}^{16}\text{O}$ fundamental mode [1.1% minority species within the $^{12}\text{C}^{16}\text{O}/\text{Ru}(001)$ layer], which displays only moderate thermal broadening. We therefore conclude that the broadening of $\nu''_{\text{C-O}}$ with increasing T is largely due to a thermally activated decay of the two-phonon bound state into two single phonon states. Detailed theoretical models have

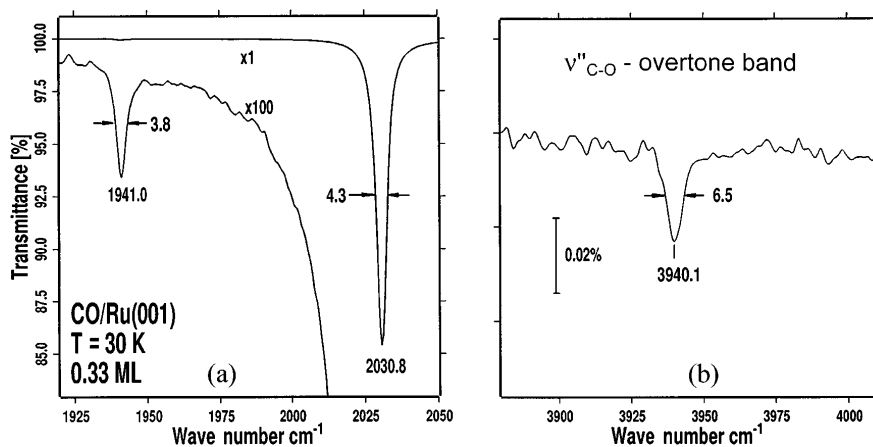


FIG. 1. (a) Infrared absorption spectra of the C-O stretching mode ν'_{C-O} of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ CO/Ru(001) layer taken at 30 K. The corresponding mode of naturally abundant $^{13}\text{C}^{16}\text{O}$ is displayed in an enlarged vertical scale; (b) ν''_{C-O} overtone band observed at about twice the frequency of the fundamental ν'_{C-O} modes.

been developed recently to describe such relaxation processes for molecular solids [12]. It is found that the decay of the bound pair of excitations is mediated by absorption of lattice phonons, a process which can be traced down to the cubic terms of the anharmonic vibrational potential.

The stability (or binding energy) of the bound state amounts to $2\hbar\omega_e x_e = 37 \text{ cm}^{-1}$ in our case. An Arrhenius analysis of the linewidth in excess of $2 \times \Gamma(\nu'_{C-O,loc})$ of the $^{13}\text{C}^{16}\text{O}$ band (the resulting value is proportional to the decay rate of the two-phonon bound state) yields an activation energy of $E_a = 170 \text{ cm}^{-1}$ which is much higher than the above mentioned value. However, an Arrhenius analysis will give the proper activation energy E_a only if $E_a \gg \hbar\omega_0$, i.e., many phonons of average energy $\hbar\omega_0$ contribute to surmount the barrier. In the case of $E_a < \hbar\omega_0$ the analysis will yield the value of the phonon which contributes most to the decay process. The found value of $150\text{--}200 \text{ cm}^{-1}$ therefore suggests that a high $k_{||}$ phonon with a correspondingly high energy is necessary to effectively split the two-phonon bound state into two (possibly propagating) single phonon states. Indeed surface phonons in the region of 220 cm^{-1} have very recently been observed for $\text{O}(2 \times 2)/\text{Ru}(001)$ [13]; no data on $(\sqrt{3} \times \sqrt{3})\text{CO}/\text{Ru}(001)$ or the clean Ru(001) surface are available.

Efforts to detect a two-phonon bound state for the fully covered CO/Ru(001) layer ($\Theta_{\text{CO}} = 0.67 \text{ ML}$) were un-

TABLE I. Line positions of the localized (singleton) C-O stretch modes ($T = 30 \text{ K}$) of $(\sqrt{3} \times \sqrt{3})R30^\circ$ CO/Ru(001). The accuracies of the line positions and the anharmonicity constants are $\pm 0.2 \text{ cm}^{-1}$ and $\pm 0.3 \text{ cm}^{-1}$, respectively.

| | Vibrational Frequencies [cm^{-1}] | | |
|---------------------|--|------------------------------|------------------------------|
| | $^{12}\text{C}^{16}\text{O}$ | $^{13}\text{C}^{16}\text{O}$ | $^{12}\text{C}^{18}\text{O}$ |
| ν'_{C-O} | 1988.6 | 1943.5 | 1943.3 |
| ν''_{C-O} | 3940.1 | 3851.4 | 3851.3 |
| $\hbar\omega_e x_e$ | 18.5 | 17.8 | 17.6 |

successful. This is attributed to the strong intermolecular coupling between the oscillators for such a dense layer which effectively prevents localization of two vibrational quanta at a single oscillator. The question of localization of vibrational energy has been examined for a number of large molecules (benzene, SF_6 , dihalomethanes) [14–16] as well as for molecular crystals [17,18]. Within the benzene molecule, for example, intermode coupling among identical C-H oscillators leads to the observation of delocalized excitations at $\nu = 1$ despite the strong anharmonicity of the C-H bonds. For higher frequency vibrational levels complete localization eventually occurs. For molecular crystals the localization problem has been related to the relative strength of the intermolecular coupling versus the intramolecular anharmonicity [18]. An equivalency between two-phonon bound

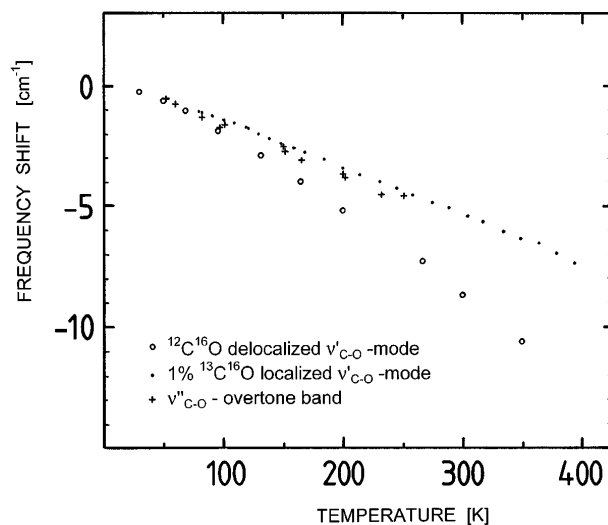


FIG. 2. Frequency shifts of the various vibrational bands with temperature: (+) ν''_{C-O} overtone band ($\times 1/2$); (•) ν'_{C-O} localized fundamental of naturally abundant $^{13}\text{C}^{16}\text{O}$; (o) ν'_{C-O} delocalized fundamental of $^{12}\text{C}^{16}\text{O}$.

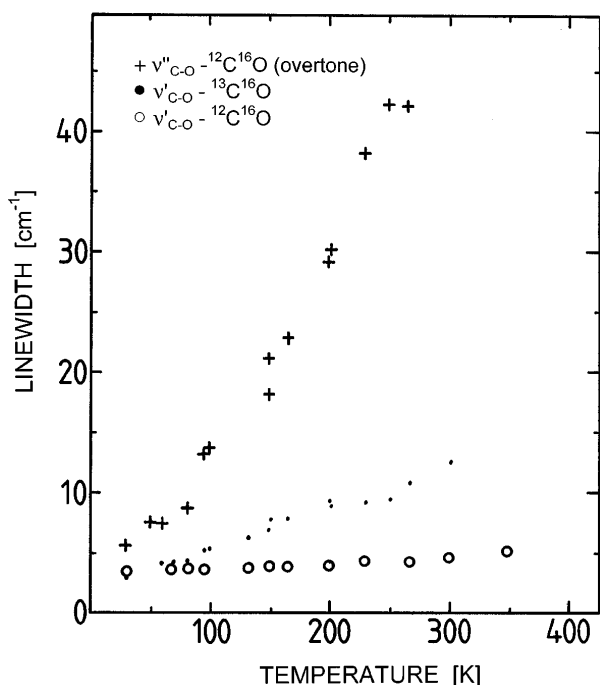


FIG. 3. Linewidths of the various vibrational bands with temperature. (+) ν''_{C-O} overtone band; (•) ν'_{C-O} localized fundamental of naturally abundant $^{13}C^{16}O$; (◊) ν'_{C-O} delocalized fundamental of $^{12}C^{16}O$. Note that the given values are derived by deconvolution of the Lorentzian line shape of the vibrational bands with the instrumental resolution function; we used a Happ-Genzel apodization function which provides a Gaussian line shape to high accuracy.

states and localized single phonon states bound to an impurity potential of strength $2\hbar\omega_e x_e$ has been suggested. Again, localization is more likely the higher the vibrational excitation level. Note that the anharmonic shift increases quadratically with the vibrational quantum number whereas the band width of a multiphonon state increases linearly with ν and the split-off of a localized overtone band is easier at high ν . In case of the fully covered CO/Ru(001) layer the bandwidth of the fundamental mode apparently is too large so that a localized two-phonon state exists only virtually and instantaneously decays into two single phonon states due to the strong intermolecular coupling induced by the oscillating dipole field. For $(\sqrt{3} \times \sqrt{3})CO/Ru(001)$ this intermolecular coupling is weaker and localization of two quanta is possible, i.e., the two phonon bound state becomes real. High temperatures then are expected to cause extra coupling to ν'_{C-O} modes with parallel momentum $k_{||} \neq 0$ through quasielastic scattering (and parallel momentum transfer) events by substrate phonons, thereby shortening the lifetime of the ν''_{C-O} mode. It is expected that for other adsorbate systems on transition metal surfaces such localized overtone vibrations will also be observed.

In conclusion, a two-phonon bound state of the fundamental C-O stretch mode has been observed for

CO/Ru(001) by infrared spectroscopy. For the first time temperature dependencies of the line positions and widths of a two-phonon bound state have been examined which suggest a thermally activated decay of this overtone band into two single phonon states. Isotopic substitution experiments have allowed the accurate extraction of the anharmonicity parameters of the internal bond of adsorbed CO which is 40% higher than found for the CO gas phase species.

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