Probing the Surface Brillouin Zone by Infrared Absorption Spectroscopy: Asymmetric Line Shape of Vibrational Combination Band

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The combination band of the C-O and the Ru-CO stretch vibrational modes of CO adsorbed on Ru(001) has been used to study vibrational dispersion effects by infrared absorption spectroscopy. For an ordered CO layer both vibrational modes can be excited far from the Γ point while fulfilling the $\mathbf{q} \approx 0$ condition through $\mathbf{q}$ vector matching. It is found that diluted layers lacking intermolecular interactions display a symmetrical and narrow line shape which broadens substantially for the $(\sqrt{3} \times \sqrt{3})R30°$CO layer and displays a pronounced asymmetry, in good agreement with theory. [S0031-9007(97)03062-7]

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Vibrational modes of adsorbate species, at low adsorbate coverages, are usually not perturbed by the adsorbate-adsorbate interactions. However, for densely packed layers this is no longer true. Here lateral interactions affect the adsorbate electronic structure, e.g., via the electrostatic Stark shifts of molecular levels due to the permanent dipoles of neighboring adsorbates, or because of the direct overlap of the molecular orbitals of nearby adsorbates. Furthermore, indirect interactions via the substrate also occur, giving rise to dispersion of the adsorbate vibrational and electronic levels.

For most adsorbate modes, especially on metal surfaces, the dipole-dipole coupling gives the dominating contribution to the dynamical coupling and dispersion of adsorbate phonons. Dipole coupling occurs for all modes (vibrational coordinate u) having a nonzero dynamic dipole moment μ_u'. The oscillating dipole field of a vibrationally excited molecule couples to the neighboring oscillators (dipoles) to cause a line shift of the $\mathbf{q} = \mathbf{0}$ phonon mode by $\Delta\omega$ [1,2]. The strength of the dipole coupling scales $\sim(\mu_u')^2$, and decays with distance like $1/\Delta R^3$, and therefore is sensitive over distances of many unit cells. As dynamic dipole coupling critically depends on the relative phase among the oscillators within an array it will produce a dispersion.

So far little attention has been devoted to dispersion effects of adsorbate vibrational modes [3–5]. The method used in early studies, high resolution electron energy loss spectroscopy (HREELS), has some drawbacks: (a) the resolution is usually of the same order of magnitude as the observed dispersion, and (b) when performing off-specular EELS, artificial line shifts due to misadjusted electron optics, or residual magnetic fields inside the spectrometer, can limit the accuracy of the analysis. Despite these constraints, the dispersion of a $c(2 \times 2)$CO/Cu(100) layer could be probed in a detailed study by Andersson and Persson [3], and a value of about 40 cm^{-1} for the bandwidth was determined. The dynamical dipole coupling gives a negative slope of the dispersion (i.e., $\omega_{\mathbf{q}}$ decreases with increasing $|\mathbf{q}|$), and yields a maximum density of states near the zone boundary.

Unfortunately, the much higher spectral resolution of infrared absorption spectroscopy (IRAS) is of no practical use for such studies since the ir photons carry only little momentum and excitation of vibrational modes occurs very close to the Γ point, i.e., at $\mathbf{q} \approx \mathbf{0}$. Efforts to probe the Brillouin zone therefore appear to be a pointless endeavor.

In the present Letter we will demonstrate that probing the vibrational band structure by IRAS becomes, in fact, feasible whenever the combined excitation of two vibrational modes is concerned. Of course, the wave-vector conservation rule is still valid but it must now be applied to the sum of two vibrational modes ω_1 and ω_2. The restriction $\mathbf{q} \approx \mathbf{0}$ now reads like $\mathbf{q}_1 + \mathbf{q}_2 \approx \mathbf{0}$ which leaves the freedom to excite the individual modes far from the Γ point at $\mathbf{q}_1 \approx -\mathbf{q}_2 \neq \mathbf{0}$. A drawback of this method is the very weak reflectivity change associated with excitation of such combination bands, and the stringent requirements on the layer homogeneity. This is why very few such studies were performed so far [6], despite the fact that the idea of probing $\mathbf{q} \neq \mathbf{0}$ modes by absorption of ir light has been known for quite some time, especially with respect to studies of molecular crystals [7,8]. By using a very stable and sensitive experimental setup [9] we have been able to study, under conditions of strong and weak lateral interactions, the line shape of the [Ru-CO + C-O] combination band of a chemisorbed CO layer on Ru(001). This system was chosen because of the high homogeneity to which the layer can be prepared. It will be shown that while the linewidth of the band is narrow and the line shape symmetrical for individual oscillators (diluted layer), a broad and asymmetric band is observed for denser layers. Taking into account the dispersion of the two fundamental modes as well as the probability of their combined excitation, we show that theoretical calculations reproduce the observed line shape well [10].

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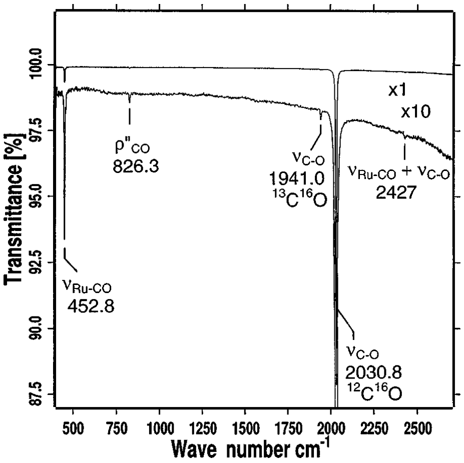

FIG. 1. Infrared absorption spectra of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ CO/Ru(001) layer taken at 30 K with 2 cm^{-1} resolution. The vertical scale of the spectrum has been enlarged by ×10 to emphasize the weaker absorption bands and to demonstrate baseline stability of the experimental setup. No smoothing or baseline corrections have been applied. The drop of the reflectivity above 1500 cm^{-1} is reproducible and associated with an interband transition of the Ru substrate.

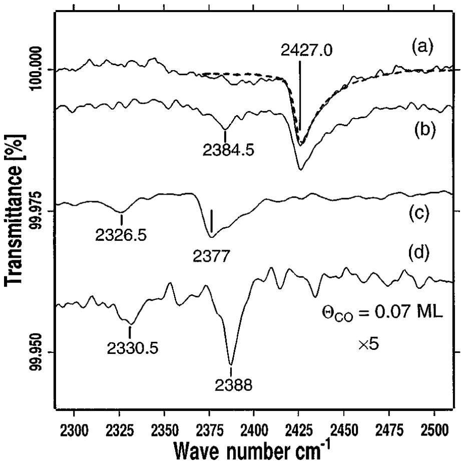

FIG. 2. Infrared absorption spectra of the [Ru-CO + C-O] combination band of various layers: (*a*) $^{12}C^{16}O$ at $\Theta_{\mathrm{CO}} = 0.33$ ML; (*b*) 90% $^{12}C^{16}O$ + 10% $^{13}C^{16}O$ at $\Theta_{\mathrm{CO}} = 0.33$ ML; (*c*) 89% $^{13}C^{16}O$ + 11% $^{13}C^{18}O$ at $\Theta_{\mathrm{CO}} = 0.33$ ML; (*d*) 89% $^{13}C^{16}O$ + 11% $^{13}C^{18}O$ at $\Theta_{\mathrm{CO}} = 0.07$ ML. The dashed curve in (*a*) has been calculated using $\delta\omega/\Delta\omega \simeq -0.04$ and $\gamma = 5\ \mathrm{cm}^{-1}$. The spectra were obtained at 30 K using a spectral resolution of 2 cm^{-1} (*a* and *b*) and 4 cm^{-1} (*c* and *d*). The slope of the baseline apparent in Fig. 1 has been adjusted to be horizontal and the spectra are offset for clarity of presentation. All layers have been annealed to 400 K before data taking.

Figure 1 displays an overview infrared absorption spectrum of a $(\sqrt{3} \times \sqrt{3})R30^\circ$ CO/Ru(001) layer ($\Theta_{\mathrm{CO}} = 0.33$ ML) taken at a temperature $T = 30$ K. A Si:B detector has been used to probe the spectral region 400–3000 cm^{-1}. The C-O band of naturally abundant $^{13}C^{16}O$ and other weak vibrational features like the overtone band of the hindered rotation (826.3 cm^{-1}) become discernible by enlargement of the vertical scale by a factor of 10. Also visible, although at poor signal-to-noise ratio, is the [Ru-CO + C-O] combination band at 2427.0 cm^{-1}, which will be discussed in more detail below.

The above-mentioned combination band has been observed for various layers containing different amounts of isotopically labeled $^{12}C^{16}O$ and $^{13}C^{16}O$ species (Fig. 2). An MCT detector has been used here to obtain spectra at considerably improved noise levels. Clearly, an asymmetric line shape with a tail on the high frequency side is observed for the majority species of the dense layers (Fig. 2, curves *a*–*c*). Note that the asymmetry is not of the Fano type, which typically would display a tail on the low-frequency side [11]. The low temperatures used in this work make sure that line broadening effects due to dephasing are virtually absent.

Layers containing a low fraction of a heavier CO isotopic species (≈10% admixture) exhibit a surprising result (Fig. 2, curves *b* and *c*). Contrary to the bands associated with the majority species the combination band of the minority species is much *narrower and displays a symmetric line shape.* This important observation excludes any mechanism responsible for the asymmetry which is unrelated to lateral coupling. Also, the line position of the $^{13}C^{16}O$ minority band (Fig. 2, curve *b*) is now located at 2384.5 cm^{-1} as compared to 2377.0 cm^{-1} found for layers containing $^{13}C^{16}O$ as the majority species (Fig. 2, curve *c*). From a physical point of view both layers differ only by their isotopic composition ratio, so that no chemical shift can be responsible for these dissimilar line positions. The measured asymmetric line shape of the combination band reflects the dispersion of the two fundamental Ru-CO and C-O modes.

This idea is corroborated by our experiments of diluted layers ($\Theta_{\mathrm{CO}} = 0.07$ ML) [12] of $^{12}C^{16}O$ (not shown) and $^{13}C^{16}O$ (containing an 11% fraction of $^{13}C^{18}O$) (Fig. 2, curve *d*). Narrow bands with a symmetric line shape are found in both cases. The dissimilar line position of the $^{13}C^{16}O$ related combination band in curves *b* and *d* of Fig. 2 is attributed to a coverage dependent chemical shift of the two component fundamental modes at CO coverages between 0.07 and 0.33 ML.

The observation of the low coverage $^{12}C^{16}O$ and $^{13}C^{16}O$ combination bands at 2438.5 and 2388.0 cm^{-1}, respectively, allows us to determine the intermode anharmonicity coupling constant $\delta\omega = \omega_{\mathrm{Ru\text{-}CO}} + \omega_{\mathrm{C\text{-}O}} - \omega_{\mathrm{comb}}$. We get $\delta\omega = 1989.9 + 446.5 - 2438.5 = -2.1\ \mathrm{cm}^{-1}$ and $1944.7 + 441.0 - 2388.0 = -2.3\ \mathrm{cm}^{-1}$ for $^{12}C^{16}O$ and $^{13}C^{16}O$, respectively (Table I). For the $(\sqrt{3} \times \sqrt{3})$-CO layer such a simple extraction of $\delta\omega$ is not possible because of the strong lateral interaction, but a full analysis (see below) also gives $\delta\omega \approx -2\ \mathrm{cm}^{-1}$ in good agreement with the results at low coverages presented above. A negative intermode coupling constant is, at first sight, unexpected, but can be understood as follows: excitation of $\omega_{\mathrm{Ru\text{-}CO}}$ will result in an increased average Ru-CO bond length

TABLE I. Line positions of the Ru-CO and C-O stretching modes as well as of the [Ru-CO + C-O] combination band obtained from a diluted layer of CO/Ru(001) at $T = 30$ K. The accuracies of the line positions and the intermode anharmonicity constants are indicated in parenthesis.

	Vibrational Frequencies $[\mathrm{cm}^{-1}]$		
	$^{12}C^{16}O$	$^{13}C^{16}O$	$^{13}C^{18}O$
$\omega_{\text{Ru-CO}}$ (± 0.3)	446.5	441.0	429 (± 1)
$\omega_{\text{C-O}}$ (± 0.1)	1989.9	1944.7	1898.1
ω_{comb} (± 0.4)	2438.5	2388.0	2330.5 (± 1)
$\Delta\omega_{\text{comb}}$ (± 0.6)	-2.1	-2.3	-3.4 (± 1.5)

which eventually leads to a free CO molecule. Since the C-O frequency of a gas phase CO is much higher (by about 200 cm^{-1}) than for the adsorbed CO, it is not unreasonable that $\omega_{\text{comb}} > \omega_{\text{Ru-CO}} + \omega_{\text{C-O}}$ so that the intermode anharmonicity is negative.

The infrared absorption profile of the combination band for the ordered $(\sqrt{3} \times \sqrt{3})$ CO structure can be calculated using the following Hamiltonian:

$$H = \sum_r \left(\frac{1}{2} m \dot{u}_r^2 + \frac{1}{2} m \Omega_0^2 u_r^2 \right) + \sum_{rs} U_{rs} u_r u_s + \sum_r \left(\frac{1}{2} M \dot{v}_r^2 + \frac{1}{2} M \omega_0^2 v_r^2 \right) + \sum_{rs} V_{rs} v_r v_s + \sum_r (A u_r^2 v_r + B u_r v_r^2 + C u_r^2 v_r^2) + H',$$

$$H' = -\mu'_u \sum_r u_r E_r - \mu'_v \sum_r v_r E_r - \mu''_{uv} \sum_r u_r v_r E_r. \tag{1}$$

Here u_r and v_r are the vibrational normal mode coordinates of the C-O and the Ru-CO stretch vibrations, respectively, of the CO molecule at site $\mathbf{x}_r$; Ω_0 and ω_0 denote the vibrational frequencies of these two modes. The lateral interactions U_{rs} and V_{rs} are assumed to be due to the dipole-dipole coupling. In (1) we have only included the most important anharmonic terms (see below). The coupling of the adsorbate to the ir electric field E is described by H' where μ'_u, μ'_v, and μ''_{uv} are derivatives of the dipole moment. There are two different processes by which the absorption of a photon can result in the excitation of the combination band: (a) direct excitation via the term $\sim \mu''_{uv} uvE$, and (b) an indirect process where the term $\sim \mu'_u uE$ (or $\sim \mu'_v vE$) first gives rise to a (virtual) excited state where only a single C-O (or Ru-CO) stretch vibration occurs, followed by the action of the anharmonicity term Au^2v (or Buv^2), resulting in a final state where both the C-O and Ru-CO modes are excited. The ir line profile can be calculated by exact diagonalization of (1) in the subspace where at most two vibrational quanta occur, i.e., we neglect those intermediate (virtual) processes where three or more vibrational quanta occur. If we furthermore assume $\Omega_0 \gg \omega_0$ (which is approximately satisfied for the C-O and Ru-CO modes), we can neglect intermediate (virtual) processes where two or zero C-O modes are excited. In this case it is easy to show that processes (a) and (b) both give contributions to the ir-absorption profile of the form

$$I(\omega) \sim \frac{1}{\{(1/n) \sum_q [1/(\Omega_{\mathbf{q}} + \omega_{-\mathbf{q}} - \omega - i\gamma/2)]\}^{-1} - \delta\omega}, \tag{2}$$

where N is the number of adsorbates, $\gamma = \gamma_1 + \gamma_2$ is the *sum* of the linewidth (FWHM) of the C-O and Ru-CO vibrational modes, and the anharmonicity $\delta\omega = -A^2 9 u_0^4 v_0^2/(\hbar^2 \omega_0) - 4C u_0^2 v_0^2/\hbar$ where $u_0^2 = \hbar/2m\Omega_0$ and $v_0^2 = \hbar/2M\omega_0$. Note that $\Omega_q = \Omega_0 + U_q$ and $\omega_q = \omega_0 + V_q$ where U_q and V_q are proportional to the spatial Fourier transforms of U_{0r} and V_{0r}. We now assume that dynamic dipole coupling is the dominant lateral interaction [13]. In this case the dipole sums U_q and V_q can be accurately approximated by quadratic functions of q (see Ref. [14]), and the sum in (2) can be calculated analytically,

$$I(\omega) \sim \frac{1}{1.2\Delta\omega/R - \delta\omega}, \tag{3}$$

where

$$R = \ln \frac{\bar{\boldsymbol{\omega}} + 0.2}{\bar{\boldsymbol{\omega}} - 1} + \frac{1}{\zeta} \ln \frac{\zeta - 1}{\zeta + 1},$$

$$\zeta = \left(\frac{0.2 + \bar{\boldsymbol{\omega}}}{1.2} \right)^{1/2},$$

where $\Delta\omega = \Delta\omega_1 + \Delta\omega_2$ is the *sum* of the dipole shifts of the C-O and Ru-CO vibrational modes and where $\bar{\boldsymbol{\omega}} = (\omega - \Omega_0 - \omega_0 + i\gamma/2)/\Delta\omega$. The bandwidth of the dipole-dipole interaction equals $1.2\Delta\omega$, and $\Delta\omega$ can be measured directly using infrared spectroscopy from isotopic mixtures.

The ir absorptance $I(\omega)$ depends only on the ratios $\delta\omega/\Delta\omega$ and $\gamma/\Delta\omega$. For CO on Ru(001) the linewidth of the C-O and Ru-CO vibrational modes are ~ 3 cm^{-1} and ~ 2 cm^{-1} so that $\gamma = 5 \pm 0.5$ cm^{-1}. The dipole shifts of the C-O and Ru-CO modes for the $(\sqrt{3} \times \sqrt{3})R30°$ layer are ~ 42 cm^{-1} and ~ 7 cm^{-1} so that $\Delta\omega \simeq 49 \pm 1$ cm^{-1}. Thus $\gamma/\Delta\omega \approx 0.1$. In Fig. 3 we show $I(\omega)$ for several different anharmonicities, and for $\gamma/\Delta\omega = 0.1$. In order to compare theory and experiment and deduce the anharmonicity $\delta\omega$ (or vice versa determine the vibrational bandwidth once we know the anharmonicity), we must know the singleton frequencies Ω_0 and ω_0. From the observed peak positions for the C-O and Ru-CO modes for the $(\sqrt{3} \times \sqrt{3})$-CO layer (2030.8 and 452.8 cm^{-1}, respectively) and from the known dipole shifts of about 42 and 7 cm^{-1}, respectively, we get $\Omega_0 \simeq 1989$ cm^{-1} and $\omega_0 \simeq 446$ cm^{-1}. Thus the difference $(\omega_{\max} - \Omega_0 - \omega_0)/\Delta\omega$, where $\omega_{\max}$ is the

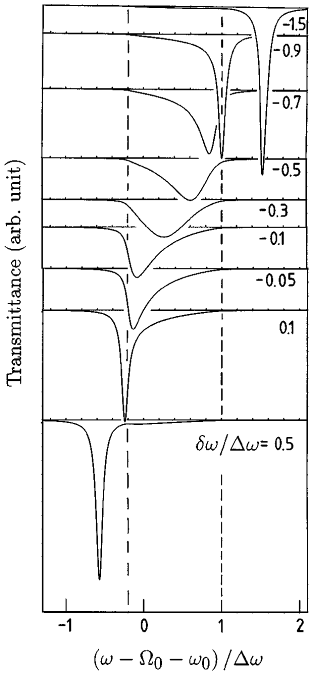

FIG. 3. Theoretical ir-absorption profiles for the combination band for several different anharmonicities $\delta\omega$, in units of the total dipole shift $\Delta\omega = \Delta\omega_1 + \Delta\omega_2$. The figure is also valid for overtones if one replaces the resonance frequencies Ω_0 and ω_0 by the singleton frequency of the fundamental. In the calculation we have assumed that the sum $\gamma = \gamma_1 + \gamma_2$, of the lifetime broadening (FWHM) of the two modes, equals $\gamma = 0.1\Delta\omega$. The dashed vertical lines mark the bandwidth of the two-phonon continuum.

frequency for which the combination has its maximum intensity, equals ≈ -0.15. Comparing this with the theoretical peak position as a function of $-\delta\omega/\Delta\omega$ (see Fig. 3) gives $\delta\omega/\Delta\omega = 0.04 \pm 0.02$, or $\delta\omega = -2 \pm 1\ \mathrm{cm}^{-1}$, in good agreement with the results derived for the dilute layers. Direct comparison of the theoretical and experimental line shapes (Fig. 2, curve *a*) allows the error bars of $\delta\omega/\Delta\omega$ to be set somewhat lower: -0.04 ± 0.01. Note that while the line shape depends on $\delta\omega/\Delta\omega$ only, the horizontal scale is a matter of the vibrational bandwidth $\Delta\omega$ alone which allows estimates of this quantity without a detailed knowledge of the anharmonicity $\delta\omega$.

It is interesting to contrast the results above for the combination band with results for the first overtone of the C-O stretch vibration [15]. The overtone occurs $\sim$20 cm^{-1} below the low-frequency edge of the two-phonon continuum $\Omega_{\mathbf{q}} + \Omega_{-\mathbf{q}}$. Thus the overtone forms a localized, split-off state, similar to the case $\delta\omega/\Delta\omega = 0.5$ in Fig. 3. In this case one expects the absorption band to have a symmetric Lorentzian-like shape, with a width equal to twice the linewidth of the fundamental C-O stretch vibration. This is indeed the case, the linewidth of the overtone being about 6 cm^{-1}, i.e., about twice the width (3 cm^{-1}) of the fundamental C-O stretch vibration. Using the theory above, which is valid also for the overtone if we replace $\omega_{\mathbf{q}} \rightarrow \Omega_{\mathbf{q}}$, we obtain an anharmonicity $\delta\omega = 2\Omega_0 - \Omega_{\text{overtone}} \approx 31\ \mathrm{cm}^{-1}$ so that $\delta\omega/\Delta\omega \approx 0.37$. Note that according to the theory there will always be some intensity in the two-phonon continuum $\Omega_{\mathbf{q}} + \Omega_{-\mathbf{q}}$, but in the present case this ir intensity is too low (see Fig. 3) to be detected in the experiment [15]. For the combination band the intermode anharmonicity is much weaker (and has a negative sign) so that no split-off state exists.

In conclusion, we have shown that asymmetric overtone/combination bands can be attributed to the excitation of $(\mathbf{q}, -\mathbf{q})$ pair of phonons of the component vibrational modes, thereby establishing IRAS as a probe of the vibrational band structure. The detailed line shape is found to depend critically on the relative ratio of anharmonicity and bandwidth associated with their combined excitation. Either of these two quantities can be determined once the other one is known.

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[9] The type of spectrometer is an evacuable Bruker 66v FTIR which has been rigidly attached to the vacuum chamber (see also Ref. [15]).

[10] As IRAS is inherently lacking in **q** selectivity a direct mapping of dispersion curves as for HREELS is not possible, of course. The $\omega(\mathbf{q})$ dispersion and the related density of states, however, are contained in the observed line shape which can be reliably calculated.

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[12] For $\Theta_{\mathrm{CO}} \leq 0.1$ ML a 2D gas of CO molecules is present while islands of $(\sqrt{3} \times \sqrt{3})R30°$ CO/Ru(001) gradually form at higher Θ_{CO}, especially at low *T*.

[13] This assumption is valid as long as the vibrational frequency is well separated from the substrate phonon bands and "through substrate" electron correlations are screened within short distances both of which is well fulfilled in our case.

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