Adsorbate-Substrate Resonant Interactions Observed for CO on Cu(100) in the Far Infrared

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Surface infrared reflection-absorption measurements for CO adsorbed on Cu(100) in the frequency range 200–500 cm^{-1} reveal, in addition to the Cu-CO stretch mode at 345 cm^{-1}, a sharp derivativelike feature at 285 cm^{-1}, assigned to the CO frustrated rotation mode which is usually dipole forbidden. Its infrared activity and Fano line shape arise from coupling to substrate electronic transitions associated with CO-induced surface states.

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Low-frequency vibrations of adsorbed atoms and molecules contain direct information on the adsorbate-substrate bond, which controls the stability, reactivity, and mobility of adsorbates. For example, the adsorption strength is related to the adsorbate-substrate stretch mode, the reactivity to a weakening of the intramolecular bond, and the diffusion to the frustrated translation mode. Spectroscopically, the details of adsorbate-substrate interactions may be reflected in the line shapes of these low-frequency modes.

Few techniques, however, can access these vibrations. Electron-energy-loss spectroscopy (EELS) has provided the most abundant information due to its particularly good sensitivity[1] below 1000 cm^{-1} (125 meV). However, its resolution (> 20 cm^{-1}) has limited its use for line shape and isotopic-shift studies. Inelastic atom-beam scattering (IABS), on the other hand, offers impressive sensitivity and resolution (typically 4 cm^{-1}), as demonstrated recently with measurements of surface phonons and frustrated translations of CO/Ni(100).[2] At present, however, this method is limited to energy transfers of less than about 250 cm^{-1} (30 meV) due to a large multiphonon background.

The usefulness of infrared spectroscopy has long been recognized[3] but its use has been hampered in this spectral region by the weak intensity of conventional blackbody sources and by the relatively strong thermal background radiation. The first measurements, based in fact on emission spectroscopy (with a cooled spectrometer), were performed by Chiang *et al.*[4] for CO on Ni(100) and Tobin and Richards[5] for CO on Pt(111). Recent instrumental developments in infrared-reflection absorption spectroscopy (IRRAS), using standard sources, have enabled several groups to extend the spectral range down to 440 cm^{-1}. In particular, measurements of the metal-carbon stretch vibration for CO on Pt(111) have been reported by Hoge *et al.*,[6] Malik and Trenary,[7] Ryberg,[8] and Persson and Ryberg[9] and on polycrystalline Ag foil by Wang and Greenler.[10] Among them, Ryberg has clearly shown that noise (instabilities and thermal fluctuations), extrinsic to the source, limits the ultimate signal-to-noise ratio achievable.

To date no infrared data have been reported for the spectral region below 450 cm^{-1}, precisely because blackbody sources are too weak (low brightness) relative to thermal fluctuations of the system. This region is, however, of particular interest since it contains most of the low-frequency frustrated vibrations of adsorbed molecules and stretch vibrations of heavy adsorbates such as alkali metals. These low-frequency modes, in close spectral proximity to the phonon band, may interact with specific substrate phonons due to anharmonic coupling. This interaction may be dominant for adsorbates on semiconductor surfaces. On metals, however, nonadiabatic coupling to electronic transitions is also possible, although originally thought to be weak at low frequencies. To study this spectral region, synchrotron radiation has an advantage as a far-infrared (FIR) source.[11] Its relative brightness compared with conventional sources in the FIR ($\approx$ 100–1000 μm) makes it a particularly attractive source for surface IRRAS spectroscopy for which small spot size and tight collimation are critical.

In this Letter, we report the first surface FIR measurements using synchrotron radiation. The vibrations associated with CO adsorbed on Cu(100) and Cu(111) are studied in the spectral region 180 to 500 cm^{-1}. In addition to the Cu-CO stretch mode at 345 cm^{-1}, we observe a sharp Fano-like mode at 285 cm^{-1}. It is suggested that this Fano resonance arises from a coupling of the normally forbidden frustrated CO rotation to an infrared absorption band. Broadband absorption measurements indicate that this band is of electronic rather than vibrational origin.

Synchrotron radiation in the spectral range from 50 to 800 cm^{-1} was analyzed by a Nicolet 20F vacuum interferometer mounted on the infrared beam line[12] U41R at the National Synchrotron Light Source with a diamond window separating the vacuum of the vacuum-ultraviolet storage ring from that of the interferometer. CsI windows mounted on the UHV chamber limit the range of measurements to above 180 cm^{-1}. After the interferometer, the collimated radiation was focused using $f/10$ optics onto a 2-cm-long Cu crystal ($\theta_{\text{inc}}=85°$), and collected and refocused into a liquid-helium-cooled, boron-doped Si bolometer. The lowest noise level achieved in a few minutes, $\Delta R/R|_{\text{noise}} \sim 0.006\%$, is still dominated by synchrotron-radiation instabilities. Additional measurements in the spectral range 800-4000 cm^{-1} were performed with a Nicolet 60SX interferometer equipped with a conventional globar source and a Hg-Cd-Te detector. The sample was cleaned by Ar^+ sputtering (0.5 keV, 1 $\mu\text{A/cm}^2$) and annealing (850 K). The surface condition was monitored by cylindrical mirror analyzer (CMA) Auger-electron spectroscopy, thermal desorption, and simultaneously by LEED and ir spectroscopy.

Figure 1 shows the vibrational spectrum associated with a $c(2\times 2)$ structure of $^{12}\text{C}^{16}\text{O}$ and the two isotopes, $^{12}\text{C}^{18}\text{O}$ and $^{13}\text{C}^{18}\text{O}$, on Cu(100). The absorptions at 345 cm^{-1} in (a), 334 cm^{-1} in (b), and 337 cm^{-1} in (c) are assigned to the Cu-CO stretch mode of CO adsorbed on top of a Cu atom, in good agreement with EELS studies by Andersson[13] and Uvdal *et al.*,[14] who report a mode at 42.5 meV (~ 343 cm^{-1}) for $c(2\times 2)$ $^{12}\text{C}^{16}\text{O}$. The isotopic shifts for $^{13}\text{C}^{18}\text{O}$ (3.2%) and $^{12}\text{C}^{18}\text{O}$ (2.3%) are consistent with those expected for a Cu-CO stretching mode. The observed FHWM is 10 ± 2 cm^{-1} in (a) and (b) and 8 ± 2 cm^{-1} in (c) from which we estimate the intrinsic linewidth to be ~ 6 cm^{-1}. Since much narrower widths are found for CO/Pt(111),[6-8] we cannot rule out the possibility that our measured width is dominated by inhomogeneous broadening. The intensity of the absorption at 345 cm^{-1}, i.e., $I_{(\text{Cu-CO})} \equiv \int (\Delta R/R) d\tilde{\nu}$, is 7×10^{-3} cm^{-1}, roughly a factor of 40 weaker than that of the corresponding C-O stretch mode at 2084.6 cm^{-1} [Fig. 2(b)]. We note that weak metal-carbon vibrations (e.g., 1/70 of the C-O stretch) have been reported for CO on Pt(111) by Hoge *et al.*[6]

The second absorption feature observed at 273 cm^{-1} for $^{13}\text{C}^{18}\text{O}$ [Fig. 1(b)] and ~ 285 cm^{-1} for both $^{12}\text{C}^{16}\text{O}$ [Fig. 1(a)] and $^{12}\text{C}^{18}\text{O}$ [Fig. 1(c)] is remarkable due to its asymmetric line shape, reminiscent of a Fano resonance.[15] The isotopic shift demonstrates that it corresponds to the frustrated rotation of CO.[13,14,16,17] Indeed, the frequency dependence of the frustrated rotation can be estimated by calculating that of the bending mode (ν_2) of the linear molecule Cu-C-O which is given by[18]

$$(2\pi\nu_2)^2 = \frac{k\delta}{l_1 l_2}\left[\frac{l_1^2}{m_{\text{O}}} + \frac{l_2^2}{m_{\text{Cu}}} + \frac{(l_1+l_2)^2}{m_{\text{C}}}\right], \qquad (1)$$

where $l_1 = d_{\text{Cu-C}} \sim 1.92$ Å, $l_2 = d_{\text{C-O}} \sim 1.18$ Å, $m_{\text{Cu}} = 63.5$, $m_{\text{O}} = 16$, and $m_{\text{C}} = 12$ amu. Thus to a good approximation, $\nu_2 \sim 1/\sqrt{m_{\text{C}}}$, accounting for the observed

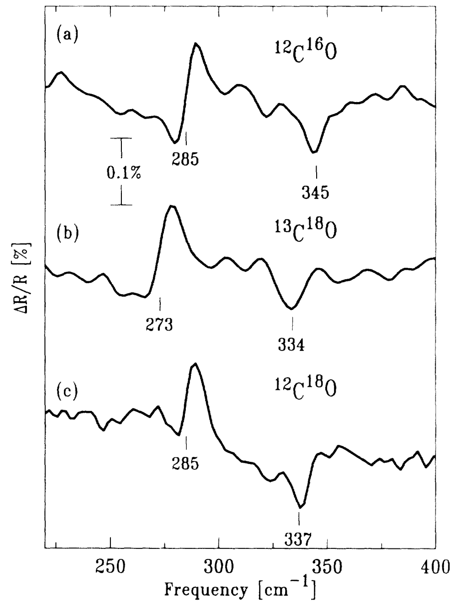

FIG. 1. Infrared-reflection absorption spectra (p polarization) of the metal-carbon stretch region for CO adsorbed in a $c(2\times 2)$ structure on Cu(100) ($\theta=0.5$ ML) at 100 K: (a) $^{12}\text{C}^{16}\text{O}$ (resolution, $\Delta\tilde{\nu}=8$ cm^{-1}); (b) $^{13}\text{C}^{18}\text{O}$ ($\Delta\tilde{\nu}=8$ cm^{-1}); (c) $^{12}\text{C}^{18}\text{O}$ ($\Delta\tilde{\nu}=6$ cm^{-1}). The spectra are obtained by averaging 750 scans resulting in a total measurement time of 6 min.

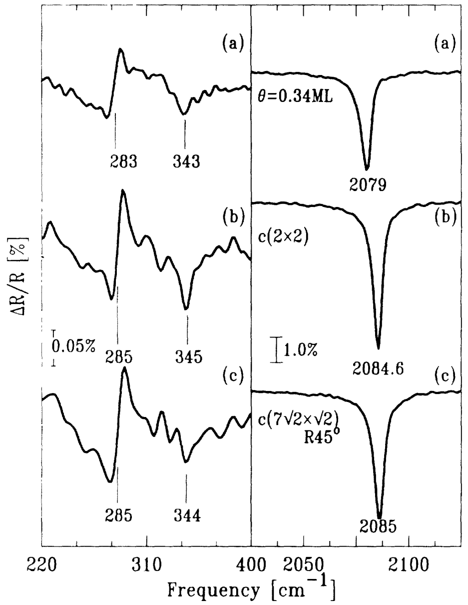

FIG. 2. Vibrational spectra for CO adsorbed on Cu(100) as a function of coverage. (a) $\theta=0.34$ ML; (b) $\theta=0.5$ ML, symmetry $c(2\times 2)$; (c) $\theta \geq 0.7$ ML, symmetry $c(7\sqrt{2}\times\sqrt{2})\text{-}R45°$. The data for the metal-carbon stretching region were taken at 8-cm^{-1} resolution using synchrotron radiation (p polarized). The data for the C-O stretch region were taken at 2-cm^{-1} resolution using a conventional (unpolarized) source.

4.2% shift for $^{13}C^{18}O$ and *the absence of a shift for* $^{12}C^{18}O$. This isotope dependence unambiguously rules out the fundamental or harmonics of the frustrated translation parallel to the surface.[2,19] In addition, a careful series of checks involving analysis of thermal desorption spectra for different surface qualities shows that the feature at 285 cm^{-1} cannot be associated with CO at surface defects.

Having assigned this mode at 285 cm^{-1} to the frustrated rotation, it remains to understand both its infrared activity and its unusual line shape. In their study of CO/Cu(100), Uvdal *et al.*[14] observe a feature between 34 and 36 meV (275–290 cm^{-1}) *only* with the appearance of a $c(7\sqrt{2}\times\sqrt{2})$-$R45°$ pattern; i.e., for a compression above $\theta=0.5$ ML. ($\theta=1$ ML is 1 monolayer or 1.5×10^{15} atoms/cm^2.) Its absence at the $\theta=0.5$ ML $c(2\times2)$ structure led the authors to conclude that the dipole activity was related to the group-site symmetry of the $7\sqrt{2}\times\sqrt{2}$ unit cell. To check whether the infrared activity is in fact related to the onset of the compression structure, we have taken data (a) at low coverage, (b) at $\theta=0.5$ [$c(2\times2)$ structure], and (c) at $\theta>0.5$ ML in the $c(7\sqrt{2}\times\sqrt{2})$-$R45°$ structure (see Fig. 2). The spectra in Fig. 2 clearly show that the mode increases in intensity throughout the coverage range and is observed independent of surface order, meaning that it cannot be related to formation of an ordered structure and, in particular, not to the compression structure. Moreover, we also observe such a mode at 281 cm^{-1} for CO adsorbed on a Cu(111) surface over the entire coverage range suggesting a more general nature of this mode.

In order to see whether this mode is related to the occupation of bridge sites we have also measured the C-O stretch region from 1700 to 2100 cm^{-1}. We observe only a single band assigned[13,20] to linearly adsorbed CO in an atop site (Fig. 2, right panel) with no absorption around 1850 cm^{-1}. (The noise level places an upper limit of 5% of a monolayer of such sites.) Furthermore, for CO/Cu(111) the mode grows linearly with the occupancy of atop sites, but does not increase further in intensity as the bridge sites become occupied. This clearly demonstrates that this mode is related to CO adsorbed on atop sites.

Infrared activity of a parallel mode (dipole forbidden in the absence of coupling) can also arise from coupling of a sharp vibrational mode to a continuum or broader infrared absorption associated either with substrate vibrations (phonons[21]) or with substrate electronic transitions.[9] An interference feature in the background absorption itself is the direct result of this coupling.[22] Such a phenomenon was observed in infrared absorption spectra for a parallel mode of H adsorbed on W(100) and Mo(100).[23(c)] The main spectroscopic difference between a phonon and electron continuum is the absorption band shape. Surface phonon bands exhibit a sharper spectrum (~50 cm^{-1}) with a negligible contribution above ~250 cm^{-1} for Cu surfaces.[24] Electronic absorption bands are usually broader (> 500 cm^{-1}, 0.05 eV) and can occur at higher frequency. Measurements of the absorption in the vicinity of the vibrational features show that a broad absorption, *associated with the CO-covered Cu(100) surface,* is observable above 200 cm^{-1} (see Fig. 3). Such an absorption cannot be associated with substrate phonons. Furthermore, the line strength and shape of the Fano features are similar for all three isotopes, even though their frequencies vary by more than 10 cm^{-1}. Both these indirect pieces of evidence suggest that the spectral feature associated with the frustrated rotation mode (Fig. 1) is observed because of its coupling to an infrared allowed electronic absorption. In effect, the vibration is not detected directly, but rather appears as a sharp feature in a broad absorption band.

Nonadiabatic coupling between the frustrated rotation and the electronic transitions measured in Fig. 3 can account for all the observations. Indeed, as argued earlier,[23(b)] infrared absorption below a metallic surface is dominated by electronic transitions *parallel* to the surface. By symmetry, such transitions can couple only to parallel vibrational modes[21(b)] such as the CO frustrated translation and rotation, and not to perpendicular modes, such as the Cu-CO stretch. Strong coupling leads to a modulation of the electronic absorption, usually with a large asymmetry, as observed in Figs. 1 and 2. In contrast, electrons cannot excite parallel electronic transitions in the specular scattering geometry due to symmetry considerations.[23(b)] Therefore, the lack of both electronic scattering (above 200 cm^{-1}) and vibrational scattering (at 285 cm^{-1}) in the EEL spectra of Andersson and co-workers[13,14,16] provides a strong confirmation of the proposed mechanism for the observation of

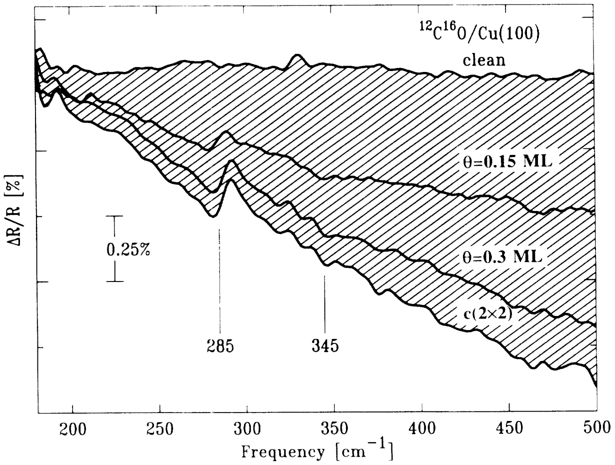

FIG. 3. Vibrational spectra for $^{13}C^{18}O$ on Cu(100) as a function of coverage, showing the changes in the background. The hatched area corresponds to an increase in electronic absorption for the CO-covered surface. To minimize time-dependent drifts, shorter averaging is performed resulting in more noisy spectra. Note that large systematic errors at very low frequencies make it difficult to determine precisely the edge of this electronic absorption.

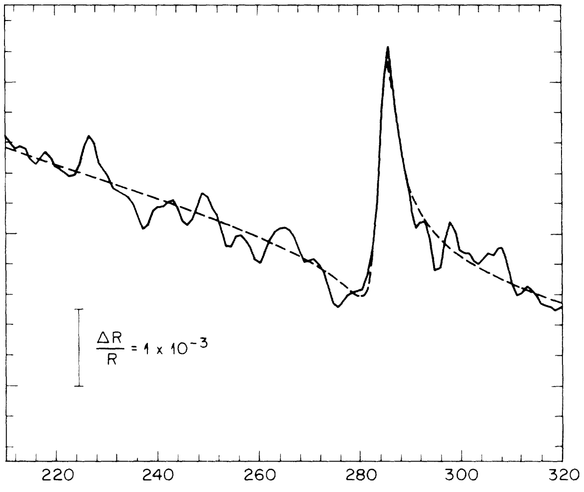

FIG. 4. High-resolution ($\Delta\tilde{\nu}=3$ cm^{-1}) spectrum of the Fano feature at 284.5 cm^{-1} for $^{12}C^{18}O$. The spectrum is obtained after removing interference features (due to the diamond window) in the interferogram before Fourier transformation. The fit to the data (dashed line) gives $\tilde{\nu}_0=284.5$ cm^{-1}, $\Delta\tilde{\nu}=4.2$ cm^{-1}, and $\tilde{\nu}_0\tilde{\tau}=-1.6$. The asymmetry ($\tilde{\nu}_0\tilde{\tau}$) is much stronger and of opposite sign to that of H on W(100), ($\tilde{\nu}_0\tilde{\tau}=+0.5$), while the width ($\Delta\tilde{\nu}=4.2$ cm^{-1}) is much smaller ($\Delta\tilde{\nu}_H=22$ cm^{-1}) [Ref. 23(b)].

the CO frustrated rotation. This argument is similar to the one used to explain the EELS data on the H/W(100) and H/Mo(100) systems.[23(b)]

With the above evidence that electronic coupling is dominant, a lower limit on the vibrational lifetime may be obtained from a fit of the Fano feature measured with higher resolution (Fig. 4). The measured width ($\sim$4 cm^{-1}) indicates that the electronic damping results in $\gtrsim$ 1-ps lifetime. We note that the large asymmetry is not consistent with a multiphonon decay. These findings provide strong support to the suggestion of Persson and Ryberg[9] that multiphonon emission is negligible compared to the excitation of electron-hole pairs, even for modes close to the phonon band.

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