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Vibrational dephasing of terminally bonded CO on Ru(001)

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The temperature-induced changes in line shape and frequency of the internal stretching mode have been studied with Fourier-transform infrared spectroscopy for terminally bonded CO on Ru(001). The data fit a dephasing model and allow us to determine the frequency of the external mode with which the energy exchange occurs. This mode is identified as the frustrated translation of the molecule parallel to the surface.

INTRODUCTION

The study of line shapes and frequency shifts of internal vibrations of molecules adsorbed on surfaces can provide important new insights into molecule-substrate and intermolecular interactions. The mechanism of homogeneous line broadening has recently stimulated much discussion. Two mechanisms have been considered, namely, electron-hole pair excitation[1-4] and vibrational dephasing.[5-8] The former leads to temperature-independent line shapes and is believed to be the dominant mechanism for the wagging mode of hydrogen on W(100) (Ref. 3) and for the C-O stretch mode of terminally bonded carbon monoxide on Cu(100).[4] In contrast, vibrational dephasing leads to temperature-dependent changes in line shape and frequency[6] and has been suggested to prevail for bridge-bonded CO on Pt(111) (Ref. 5) and Ni(111).[8] The difference between Cu(100) and Ni(111), it has been argued,[7,8] can be found in the difference between the terminal- and bridge-bonding site.

In this Brief Report we demonstrate in the case of Ru(001) that vibrational dephasing can be found for terminally bonded CO and that it exhibits distinctly different behavior from that of bridge-bonded molecules. By comparing our data with a theoretical dephasing model we determine the frequency of the exchanging mode to be 105 cm^{-1} and identify this mode as the frustrated translation of the molecule parallel to the surface.

The experiments were performed in an ultrahigh vacuum chamber (10^{-11} Torr range) equipped for infrared spectroscopy, low-energy electron diffraction, Auger spectroscopy, and thermal desorption measurements. Experimental procedures, preparation, and cleaning of the ruthenium crystal have been described earlier in detail.[9] Infrared spectra were obtained with a rapid-scanning Perkin-Elmer 1800 Fourier-transform infrared spectrometer in single-reflection mode with 80° angle of incidence. Vibrational spectra were obtained by adding 32 scans in a total measurement time of 100 sec and comparing against a stored background spectrum of the clean surface. The $\sqrt{3}\times\sqrt{3}R30°$ structure of CO on Ru(001) has been chosen because *all the molecules are adsorbed in identical on-top sites.*[11] This ensures the absence of temperature-induced changes in adsorption sites[5] or intensity transfer between different adsites.[8] Furthermore, the coverage of $\Theta=0.33$ gives a sufficiently large CO-CO spacing (4.3 Å) to minimize intermolecular interactions. In order to prevent inhomogeneous line broadening careful control of the CO coverage was necessary to obtain a well-ordered adlayer. Saturation of the $\sqrt{3}\times\sqrt{3}R30°$ structure was experimentally verified by observation of the corresponding low-energy electron diffraction pattern, saturation of the first thermal desorption state,[10] and the vibrational line shape and frequency of the C-O stretch mode.[11] Infrared spectra of the C-O stretch region for a $\sqrt{3}\times\sqrt{3}R30°$ layer on Ru(001) are shown in Fig. 1. (a) The line shapes of the absorption bands at 300 K and (b) after cooling to 80 K are nearly symmetrical and thus indicate the absence of inhomogeneous broadening. The latter, caused by disordering or incomplete ordering of the adlayer, usually leads to asymmetries in the peak shape.[4,12] We note also the absence of a high-frequency tail of the line shape. The latter was observed for CO/Cu(100) by Ryberg[4] and seen as evidence for electron-hole-pair-induced line broadening. The spectra in Fig. 1 can be fitted very well to a Lorentzian distribution (broken line in Fig. 1) but not to a Gaussian (dotted line in Fig. 1). This clearly indicates that the line shape is truly homogeneous. The spectra in Fig. 1 also reveal temperature-dependent changes in the C-O stretch frequency and an increase in the linewidth. Figure 2 shows the *reversible* frequency shift between 80 and 425 K and the corresponding change in linewidth, which has been corrected for instrumental resolution (2.4 cm^{-1}).

The experimental data presented above can be explained by a theoretical model which we now discuss (see Ref. 13 for more details). The frequency Ω of the internal C-O stretch vibrational mode depends on the bonding position on the surface. This variation with bonding position will, at temperatures where the molecules are mobile, lead to a broadening of the vibrational line. Let us assume that the C-O stretch vibration couples anharmonically to mainly one (low frequency) frustrated rotation or translation. Let Q denote the normal mode coordinate for this mode. We then have

$$\Omega^2=\Omega^2(Q)\cong\Omega_0^2+aQ^2\ ,$$

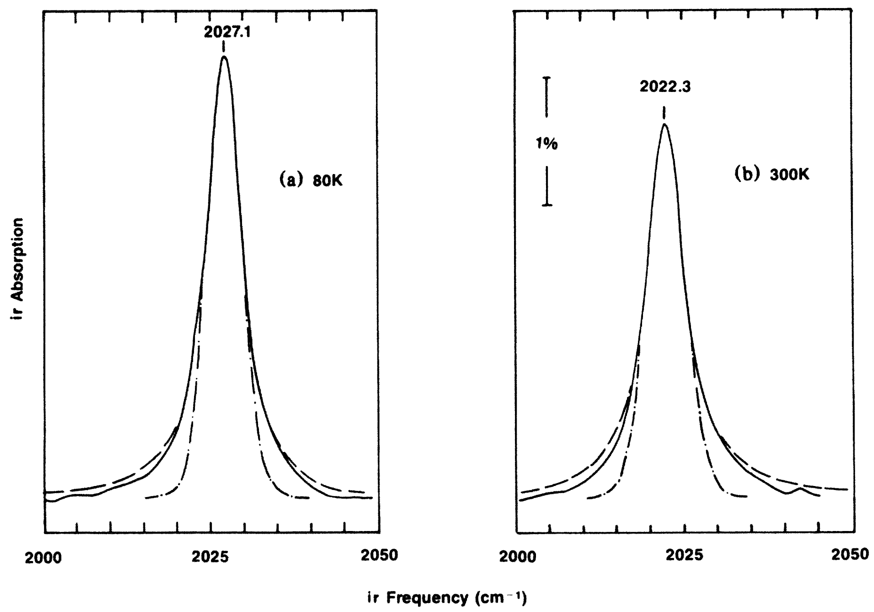

FIG. 1. (a) Infrared spectra of the internal C-O stretch for a $\sqrt{3}\times\sqrt{3}R30°$ layer of CO on Ru(001) at 300 K and (b) after recooling to 80 K. The spectra (solid lines) show raw data with 32 scans each at 2.4 cm^{-1} resolution. A comparison of Lorentzian (broken lines) and Gaussian (dotted lines) fits indicates that the line shape is Lorentzian and thus homogeneous.

where we have made use of the fact that the system is symmetric as $Q \longrightarrow -Q$. If $u_i(t)$ denotes the normal mode coordinate for the C-O stetch vibration of molecule i, then the equation of motion for this coordinate is

$$m^*\ddot{u}_i + m^*(\Omega_0^2 + aQ_i^2)u_i + \sum_j{}' t_{ij}u_j = 0 \ . \tag{1}$$

The last term in this equation represents the dipole-dipole interaction between the molecules and was neglected in an earlier treatment (Ref. 14). We note that t_{ij} is not the direct dipole-dipole coupling interaction but is screened by the electronic polarizability α_e of the adsorbed molecules. That is, if t_q denotes the spatial Fourier transform of t_{ij} then

$$t_q \sim U_q/(1+\alpha_e U_q) \ ,$$

where U_q is the spatial Fourier transform of the dipole field $U_{ij} \sim |x_i - x_j|^{-3}$ + image contribution. The equation of motion for Q_i is treated quantum mechanically[13] but the basic physics is contained already in the classical limit where

$$m\ddot{Q}_i + m\omega_0^2 Q_i + m\eta\dot{Q}_i + m^* a u_i^2 Q_i = f_i(t) \ , \tag{2}$$

where the random force $f_i(t)$, in accordance with the fluctuation-dissipation theorem, must satisfy

$$\langle f_i(t) f_j(0)\rangle = 2\eta m k_B T \delta(t)\delta_{ij} \ .$$

Three important parameters enter in (1) and (2), namely, the exciton band width, $\Delta\Omega \sim \Omega_0 \alpha_v U_0/2(1+\alpha_e U_0)$ (where $U_0 = U_q$ for $q=0$ and α_v is the vibrational polarizability) the friction parameter, η, and the anharmonic coupling parameter, $\delta\omega \sim a$ ($\delta\omega$ is the change in the C-O stretch frequency, $\Omega_0 \longrightarrow \Omega_0 + \delta\omega$, as the low frequency mode Q is excited to its first excited state).

The experimental data presented in Fig. 2 are characterized by a small increase in linewidth and a large frequency shift. This is due to motional line narrowing, which can either occur if $\eta \gg \delta\omega$ *or* if $\Delta\Omega \gg \delta\omega$. As will be seen below, only the second possibility can give a consistent explanation of the experimental data.

The solid lines in Fig. 2 present calculations based on the theoretical treatment described above and in more de-

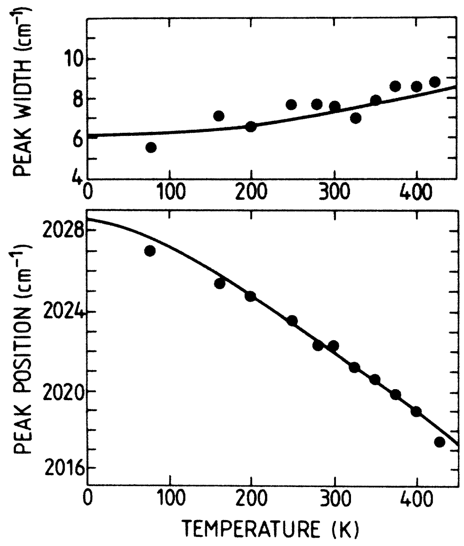

FIG. 2. C-O stretch frequency and linewidth (FWHM) as a function of temperature. The linewidth has been corrected for the instrumental resolution of 2.4 cm^{-1}. The solid lines are theoretical calculations, as described in the text, using $\omega_0 = 105$ cm^{-1}, $\delta\omega = -6$ cm^{-1}, and $\eta = 6$ cm^{-1}.

tail in Ref. 14. Including dipole-dipole interactions and using the values $\omega_0 = 105$ cm^{-1}, $\eta = 6$ cm^{-1}, and $\delta\omega = -6$ cm^{-1} we obtain very good agreement between the theoretical curve and the experimental data. From the value of the exchanging mode $\omega_0 = 105$ cm^{-1} we conclude that the frustrated translation parallel to the surface must be responsible for the dephasing process. The two remaining external *M*-CO modes (*M* represents a metal atom) are substantially higher in frequency and thus not accessible. From high-resolution electron-energy-loss spectroscopy we find 445 cm^{-1} for the *M*-CO stretch mode and 410 cm^{-1} for the *M*-CO bending mode (frustrated rotation).[15,16] Both values agree well with theoretical estimates given by Richardson and Bradshaw.[17] These authors find for on-top CO on Ni(100) values of 437 cm^{-1} for the mode Ni-CO stretch, 411 cm^{-1} for the Ni-CO bend, and 82 cm^{-1} for the frustrated translation parallel to the surface. Taking into account the larger binding energy of CO on Ru(001) compared with Ni, we expect a stiffening for the frequency of the frustrated translation parallel to the surface. Thus the value of 105 cm^{-1} which we find from our data for this mode is very reasonable.

The value $\eta = 6$ cm^{-1} for the damping of the frustrated translation is also in agreement with a rough estimate obtained from the elastic continuum model which gives[14]

$$\eta \cong (3/8\pi)(m/\rho)(\omega_0/c_T)^3\omega_0 \; , \qquad (3)$$

where $m = 28$ u is the mass of the CO molecule, $\rho = 12\,200$ kg/m^3 the density, and $c_T = 4300$ m/s the transverse sound velocity of ruthenium. We obtain $\eta = 5.5$ cm^{-1} which is consistent with the value of 6 cm^{-1} required to fit the data. The vibrational and electronic polarizabilities used in the analysis above have been obtained[18] from ir measurements by Pfnur *et al.*;[11] $\alpha_v = 0.28$ Å^3, $\alpha_e = 2.8$ Å^3, and $U_0 = 0.17$ Å^{-3}. This corresponds to an exciton band width $\Delta\Omega \sim 30$ cm^{-1}. Thus $\Delta\Omega \gg \delta\omega$, and the motional narrowing is due to the dipole-dipole coupling. Indeed, in the absence of lateral interactions ($\Delta\Omega = 0$) the above values for $\delta\omega$ and η would give an increase in the linewidth which is very similar in magnitude to the frequency shift. By performing measurements in the isotopic dilution limit[12] (where dipole-dipole interactions can be minimized) it should be possible to study the influence of the lateral interaction on the line profile. If we neglect dipole-dipole interactions, the theoretical fit to the experimental data requires a different set of parameter values, namely, $\eta = 80$ cm^{-1}, $\delta\omega = -5.5$ cm^{-1}, and $\omega_0 = 130$ cm^{-1}. In this case the dipole-dipole interaction is unimportant (and can be neglected) and the motional narrowing occurs because $\eta \gg \delta\omega$. The low-frequency mode has a similar value as above and it is still reasonable to assign it to the frustrated translation parallel to the surface. However, the damping parameter $\eta = 80$ cm^{-1} needed to fit the data is unphysically large and neither agrees with our earlier estimate [13 cm^{-1} from Eq. (3)] nor with recent measurements for CO on Pt(111) by Lahee, Toennies, and Woell[19] ($\eta < 10$ cm^{-1}). Thus we conclude that the motional narrowing must be caused by the dipole-dipole interaction.

The comparison of the dephasing behavior for linearly and bridge-bonded CO is most noticeably contrasted by the different nature of the exchanging modes and the opposite direction of the frequency shift. Persson and Ryberg[14] find for bridge-bonded CO on Ni(111) a value of $\omega_0 = 220$ cm^{-1}, which is assigned to the frustrated rotation of the molecule. In addition, they observe a blue shift in the C-O stretch frequency as well as a stronger line broadening ($\delta\omega = +34$ cm^{-1}, $\eta = 37$ cm^{-1}). These differences can be understood qualitatively in terms of the different nature of the *M*—CO bond for these two adsorption sites. For the bridge site the frustrated rotation (out of plane) is much softer (184 cm^{-1}) (Ref. 17) than for the on-top site (411 cm^{-1}) (Ref. 17). Since the former is still below the highest phonon frequency of the Ni substrate, it is now accessible as an exchanging mode. Moreover, the bridge site exhibits considerable backbonding of metal charge density into the $2\pi^*$ molecular orbitals of CO. The strongly antibonding character of these orbitals with respect to the C—O bond thus accounts for the strong dephasing behavior observed. In contrast, for the on-top site of CO on Ru(001) backbonding is much weaker. The molecule is situated farther away from the surface as indicated by a higher frequency of the C-O stretch mode of typically 100 cm^{-1} in comparison to the bridge site. This leads to the observed weaker dephasing and red shift ($\delta\omega = -6$ cm^{-1}), since excitation of the frustrated translation of the molecule parallel to the surface will move the average position of the molecule in the direction of the bridge site.

In conclusion, we find that the distinctly different dephasing behavior for on-top CO in comparison to bridge-bonded CO results from the different nature of these two adsorption sites, namely, the drastically different vibrational normal mode spectras and the stronger $2\pi^*$ backbonding in the bridge position. We note finally, that the possibility to be able to study the low-frequency frustrated translations and rotations is very important since these are the modes which first are thermally excited and therefore important in catalytic reactions and other dynamical processes at surfaces.

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