

Vibrational Phase Relaxation at Surfaces: CO on Ni(111)

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The temperature dependence of the internal stretch vibrational mode of CO adsorbed on Ni(111) has been studied by infrared spectroscopy. The results are successfully analyzed by a model for vibrational phase relaxation. It is found that anharmonic coupling between the C-O stretch mode and a low-frequency frustrated rotation gives the dominant contribution.

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Much work has been done towards an improved understanding of what determines the vibrational linewidth of molecules adsorbed on a surface. Presently, there exists an intense discussion about the relative importance of energy and phase relaxation.¹ In general, the relative importance of energy and phase relaxation is quite different at metal surfaces and at the surfaces of nonmetals, or in solids and liquids. The reason is that in the latter case energy relaxation of a high-frequency (Ω) mode can only occur via multiphonon emission, while for adsorbates on a metal surface the additional decay path caused by electron-hole-pair excitation exists. This latter mechanism is particularly important for high-frequency modes since the phase-space for electron-hole pair excitation is proportional to Ω .

Several experimental line-shape studies of vibrational modes of molecules adsorbed on metal surfaces have been published.²⁻⁷ In a recent paper,⁸ we have shown that the C-O stretch vibration of CO on a Cu(100) surface has a temperature-independent Lorentzian line shape with a width (full width at half maximum) of 4.5 cm^{-1} . This linewidth is caused by vibrational energy relaxation, most likely due to decay via excitations of electron-hole pairs. Decay via phonon emission is also possible but energy conservation requires that at least eight phonons are emitted and such high multiphonon processes have small probability. On the other hand, for low-frequency modes, such as the Ni-CO vibration on Ni(100), decay via two-phonon emission is energetically possible and probably the relevant energy relaxation process. Chiang *et al.*⁶ found at room temperature a linewidth of 15 cm^{-1} for the Ni-CO vibrational mode, which agrees well with theoretical predictions.^{9,10}

Recently, Hayden and Bradshaw⁵ have reported a strong temperature dependence of the line shapes for the C-O stretch vibrational mode on Pt(111). Similarly, Trenary *et al.*⁷ find a strong temperature dependence in the linewidth for CO on Ni(111). This tem-

perature dependence cannot be due to multiphonon emission which has negligible probability. Furthermore, damping via electron-hole-pair excitation is practically temperature independent. Thus, one must suspect that the temperature dependence of these vibrational lines is caused by vibrational phase relaxation. In this Letter, we will discuss this problem in more detail and present a combined experimental-theoretical study for the system CO on Ni(111) which clearly reveals the nature of the phase relaxation process involved.

The infrared spectrometer has been described elsewhere.¹¹ The Ni crystal was oriented, polished, and cleaned by standard procedures. The adsorption stages of CO/Ni(111) followed in general the work by Erley, Wagner, and Ibach¹² At temperatures below 300 K an ordered $c(4 \times 2)$ structure was found, with all molecules in the bridge position [Fig. 2(a)]. In Fig. 1, we present peak position and width of the internal stretch vibrational mode as function of temperature. The widths were determined by integration of the first-derivative spectra, taken with a modulation amplitude of less than $\frac{1}{10}$ slit width. A typical derivative spectrum is also shown (after signal averaging for 5 min and subtraction of the measured background). The spectrometer resolution was 2.8 cm^{-1} , which has been subtracted. The data presented are the mean value of four different depositions at each temperature with a standard deviation as error bar.

To understand the behavior shown in Fig. 1 we consider the following problem: A diatomic molecule AB is adsorbed on a metal surface. The frequency Ω of the internal $A-B$ stretch vibrational mode depends on the bonding position on the surface (for CO, Ω increases typically by 10% when going from bridge to on-top position). This variation with position will, at temperatures where the molecules are mobile, lead to a broadening of the vibrational line.

Let us assume that the $A-B$ stretch vibration couples anharmonically to mainly one (low-frequency) frus-

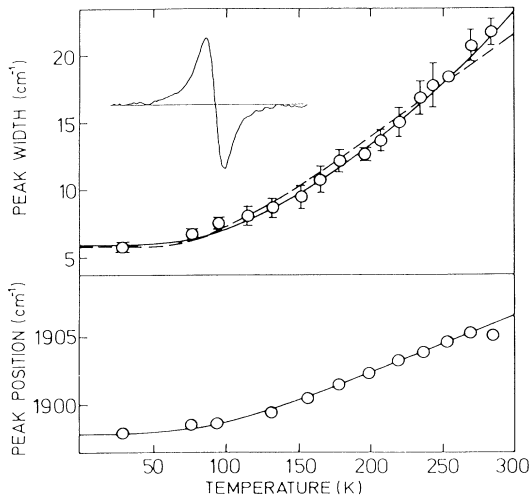


FIG. 1. The infrared-absorption peak position and width (full width at half maximum) as a function of temperature for the internal C-O stretch vibrational mode of bridge-bonded CO on Ni(111). Inset: typical first-derivative spectrum. The full and dashed curves are theoretical calculations as described in the text.

trated translation or rotation. Let Q denote the normal-mode coordinate for this mode. We then have

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

where we have assumed that the system is symmetric as $Q \rightarrow -Q$. If $u(t)$ denotes the normal-mode coordinate for the A - B stretch then the equation of motion for this coordinate is

$$m^* \ddot{u} + m^*(\Omega_0^2 + aQ^2)u = 0. \quad (1)$$

The equation of motion for the coordinate Q is taken to be

$$m\ddot{Q} + m\omega_0^2 Q + m\eta\dot{Q} + m^*au^2 Q = f(t), \quad (2)$$

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

$$\langle f(t)f(0) \rangle = 2\eta mk_B T \delta(t).$$

The physical origin of the friction force, $-m\eta\dot{Q}$, in (2) is that the Q motion is damped as a result of excitation of phonons (and electron-hole pairs).

Our basic problem is now to calculate, from (1) and (2), the line-shape function

$$I(\omega) \sim \int dt e^{i\omega t} \langle u(t)u(0) \rangle, \quad (3)$$

where the angular brackets stand for thermal average. Simple analytical expressions for $I(\omega)$ have only been found in two limiting cases: At high temperatures and for large friction $I(\omega)$ is a Lorentzian

$$I(\omega) \sim \frac{\gamma/2}{(\omega - \Omega_0 - \Delta\omega)^2 + (\gamma/2)^2},$$

where the linewidth (full width at half maximum) γ and the frequency shift $\Delta\omega$ are given by¹³

$$\gamma = \frac{2\delta\omega^2}{\eta} \left(\frac{k_B T}{\omega_0} \right)^2, \quad \Delta\omega = \delta\omega \frac{k_B T}{\omega_0}. \quad (4)$$

For low temperatures, Harris, Shelby, and Cornelius¹⁴ have shown that $I(\omega)$ is an approximate Lorentzian with

$$\gamma = 2 \frac{\delta\omega^2}{\delta\omega^2 + \eta^2} \eta e^{-\beta\omega_0},$$

$$\Delta\omega = \frac{\eta^2}{\delta\omega^2 + \eta^2} \delta\omega e^{-\beta\omega_0}. \quad (5)$$

Thus both γ and $\Delta\omega$ exhibit an activated low-temperature dependence. In the equations above, $\delta\omega = \hbar a/2m\Omega_0\omega_0$ is the frequency shift of the high-frequency mode ($\Omega_0 \rightarrow \Omega_0 + \delta\omega$) when the low-frequency mode is in its first excited state. In the general case of arbitrary $\delta\omega$, η , and T no simple analytical expression for $I(\omega)$ has been found and so it must be calculated by numerical methods.¹³⁻¹⁵

If the frequency ω_0 of the Q motion is below the maximum phonon frequency of the metal, then this vibration becomes a resonance with a width ($\sim \eta$) determined by the rate of one-phonon emission. We have assumed that η is frequency independent. However, in general, η is expected to be frequency dependent and we have recently¹⁵ derived an expression for $I(\omega)$ which is valid for arbitrary $\eta(\omega)$. Our derivation is based on a treatment by Brenig and Schönhammer¹⁶ of the Anderson Hamiltonian and consists of calculation of the phonon propagator by use of a projection operator technique. The anharmonic coupling between the u and Q modes is treated exactly while the coupling between the Q mode and crystal phonons is treated to second order when calculating the phonon self-energy. For fermions (i.e., the Anderson Hamiltonian), this is known to give an accurate solution for the propagator¹⁶ and is also likely to do so for bosons. We note that in the Markoff approximation our result reduces to that of "Anderson's random-frequency model"¹⁷ which, for low temperatures, has been studied by Harris, Shelby, and Cornelius¹⁴ [Eq. (5)]. The solid lines in Fig. 1 are calculated by use of this theory with $\omega_0 = 210 \text{ cm}^{-1}$ and $\delta\omega = 30 \text{ cm}^{-1}$ and with $\eta(\omega) \sim \rho_b(\omega)/\omega^2$, where $\rho_b(\omega)$ is the bulk phonon density of states (ω_0 is so large in the present case that surface phonon modes cannot be directly involved). The dashed curve in Fig. 1 has been calculated with a frequency-independent η (the Markoff approximation), $\eta = 37 \text{ cm}^{-1}$, and with $\omega_0 = 220 \text{ cm}^{-1}$ and $\delta\omega = 34 \text{ cm}^{-1}$. The agreement between theory and experiment is very good. We note that for low enough temperatures, the low-frequency mode ω_0 is frozen out so that $\Delta\omega$ and γ become practically temperature

independent. This low-temperature value of γ determines an upper limit to the vibrational damping rate caused by electron-hole-pair excitation. A width of about 6 cm^{-1} is much smaller than has previously been reported on transition metals and only 30% larger than for CO on Cu(100).³

Let us now discuss the implications of the values of the parameters ω_0 , η , and $\delta\omega$ found above. Richardson and Bradshaw¹⁸ have performed a normal-mode analysis of CO on a small Ni cluster. Of all the normal modes involving bridge-bonded CO, only the frustrated translation ω_{tra} and the frustrated rotation ω_{rot} (see Fig. 2) have resonance frequencies below the maximum Ni phonon frequency ($\approx 290 \text{ cm}^{-1}$). The calculated frequencies should only be taken as rough estimates, but $\omega_0 = 210 \text{ cm}^{-1}$, which we obtained by comparing theory and experiment, is close to the calculated $\omega_{\text{rot}} = 184 \text{ cm}^{-1}$ while it is a factor of 3 larger than $\omega_{\text{tra}} = 76 \text{ cm}^{-1}$. Thus we argue that in the present case the vibrational phase relaxation involves coupling to the frustrated rotation ω_{rot} . The friction coefficient η can be obtained from a lattice-dynamic calculation. We have estimated¹³ η using a continuum model for the metal and find $\eta \sim 50 \text{ cm}^{-1}$ which is consistent with the value of $\eta = 37 \text{ cm}^{-1}$ required to fit the data.

It is not possible to estimate $\delta\omega$ theoretically without an extensive chemisorption calculation, which is not yet available. However, it should be possible to make an independent experimental determination of $\delta\omega$ (and ω_0): The anharmonic coupling $\sim aQ^2u^2$ between the low- and high-frequency modes gives rise to combination bands at $\Omega_0 \pm 2\omega_0$. Theory predicts¹⁵ that at low temperatures the intensity of the line at $\approx \Omega_0 + 2\omega_0$ is a fraction $\Delta = (\delta\omega/\omega_0)^2/8$ of the intensity of the C-O stretch mode. With $\delta\omega = 30 \text{ cm}^{-1}$ and $\omega_0 = 210 \text{ cm}^{-1}$, one gets $\Delta \approx 3 \times 10^{-3}$.

An important question is why the phase relaxation is so strong for bridge-bonded CO, while it is not observed for the *terminal bonded* molecules.^{7,13} One can give qualitative arguments for $\delta\omega$ being smaller in the on-top position.^{7,13} More important, the frustrated rotation has stiffened¹⁸ to $\omega_{\text{rot}} = 411 \text{ cm}^{-1}$, which is well

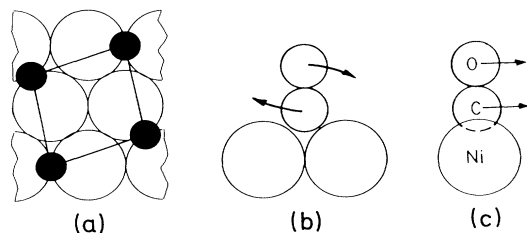


FIG. 2. (a) The position of the bridge-bonded CO molecules in the $c(4 \times 2)$ structure on Ni(111). (b) Schematic picture of the frustrated rotation, $\omega_{\text{rot}} \approx 184 \text{ cm}^{-1}$. (c) The frustrated translation, $\omega_{\text{tra}} \approx 76 \text{ cm}^{-1}$.

above the highest phonon frequency of Ni. Thus we expect the damping to be considerably smaller than for CO in the bridge position. The small magnitudes of $\delta\omega$ and η and the large magnitude of ω_{rot} (corresponding to a temperature of about $\approx 600 \text{ K}$) explain why the phase relaxation is so much weaker in the on-top position. On the basis of estimates of $\delta\omega$ and η for the low-frequency *frustrated translations* one can also understand why these modes give in general a negligible contribution to the phase relaxation process.

The vibrational phase relaxation process discussed above is, of course, not the only possible one. For example, the C-O stretch vibration is coupled *directly* to the metal substrate via the anharmonic metal-CO binding potential and this coupling gives a contribution to the vibrational phase relaxation process as has been discussed in detail elsewhere.¹⁰ For the CO/Ni(111) system, one can estimate that the contribution to the room-temperature linewidth of the C-O stretch from this coupling is $\sim 0.1 \text{ cm}^{-1}$, i.e., an entirely negligible contribution.

The lateral interaction between adsorbed CO molecules will also give a contribution to the vibrational linewidth. This process is similar to the collisional broadening occurring in a gas of molecules. For an ordered system of adsorbed CO molecules, one must, in general, account both for the long-range dipole-dipole interaction as well as for the short-range (usually repulsive) interaction between two nearby molecules. It is easy to show that the dipole-dipole interaction gives a negligible contribution to the linewidth, but the contribution from the short-range interaction is harder to estimate since much less is known about its nature.

The present authors have, in several earlier works, strongly emphasized the importance of energy relaxation via electron-hole-pair excitation.^{8,19} This was based on our experience with the system CO/Cu(100), where the line profile is essentially temperature independent. However, it is now known that in some cases, such as the system considered above, a strong temperature dependence is observed which indicates that an additional mechanism, namely, vibrational phase relaxation, comes into play. The importance of this latter process has already been suggested by others,^{1b,5,7} and is confirmed by our analysis. In particular, we have shown that under circumstances likely to prevail for bridge-bonded CO this mechanism dominates over the electron-hole mechanism at high temperatures. Nevertheless, phase relaxation gives negligible contribution for temperatures $\leq 50 \text{ K}$ so that energy relaxation via electron-hole-pair excitation is still the dominant damping mechanism of high-frequency vibrations, as $T \rightarrow 0$.

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