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Vibrational line shape of chemisorbed CO

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The width and shape of the infrared absorption peak of the internal stretch vibrational mode of CO adsorbed on a Cu(100) and a Ni(111) surface have been studied. On Cu(100) there is no temperature dependence of the width in the 20–130 K range, indicating that thermally excited low-frequency modes are not involved in the peak-broadening process. A peak-shape analysis showed that the broadening is predominantly homogeneous for the ordered $c(2\times2)$ structure and hence that the width is a true measure of the vibrational lifetime. Comparison is made to recent line-shape theories.

A fundamental property of a molecule adsorbed on a metal surface is the interaction between its vibrational modes and excitations in the metal, such as electron-hole pairs and phonons. The finite vibrational lifetime τ, due to the energy dissipation into the metal, gives rise to a width Δ to the vibration frequency. If we probe a *single* adsorbed molecule with an instrumental resolution much higher than Δ, then to first approximation the infrared absorption peak will have a Lorentzian shape with a full width at half maximum (FWHM) of $\Delta = 1/(2\pi\tau)$. However, normally we have to consider an *ensemble* of adsorbed molecules. If a considerable dynamical interaction exists between the vibrational mode and other vibrational modes (within the same molecule, in other adsorbed molecules, in the metal-molecule bond or in the metal), this will in general give rise to an increased peak width. Some time ago we made an investigation[1] of the linewidth of CO adsorbed on a Cu(100) surface at 100 K, which led to what we then thought were rather definite conclusions about the peak-broadening mechanism, namely, that it was a measure of the vibrational lifetime. However, we must admit that at that time we were not aware of other peak-broadening mechanisms that could play an equally important role. These other possibilities have been pointed out in several recent theoretical papers. In addition to the width, the different peak shapes that should be observed if a careful, high-resolution experimental determination of the absorption spectrum can be made have also been discussed. If we consider an ordered adsorbate layer the following mechanisms should be considered:

Inhomogeneous broadening. If there exists an interaction between the molecules (direct or indirect via the substrate), disorder in the adsorbate layer will produce, in the first approximation, a Gaussian-shaped peak. However, if the lateral interaction gives rise to a substantial coverage-dependent shift, the inhomogeneously broadened peak will be asymmetric. An interaction that gives an upward frequency shift for increasing coverage, like the dipole-dipole interaction, will produce a low-frequency tail[2] and vice versa.

Phase relaxation. If there exists a dynamical coupling between the considered vibrational mode and other, low-frequency modes, this will, at temperatures where the latter are excited, cause fluctuations in the normal-mode frequency and hence give rise to additional broadening.[3–6] The most important feature of this mechanism is its strong temperature dependence and that it vanishes at low temperature.

Energy relaxation. For high-frequency modes like the internal stretch of CO, the most probable vibrational damping process is via electron-hole pair excitations in the metal. The question has been whether these are excited by the long-range oscillating dipole field of the molecules[7,8] or by charge oscillations between a molecular ($2\pi^*$) resonance around the Fermi level and the conduction band.[8] To first approximation the electron-hole pair mechanism produces a temperature-independent Lorentzian peak. However, the interaction between the vibrational excitation and the quasicontinuum of electron-hole pairs should produce a high-frequency tail.[3] Furthermore, accepting the picture of a $2\pi^*$ resonance at the Fermi level, the charge oscillation between the molecule and the metal during the vibration is not instantaneous (nonadiabatic), so the charge is not in phase with the external field. This can also give rise to an asymmetric peak, with a tail in either direction depending on certain parameters.[9]

It is the purpose of this paper to present the first careful experimental determination of the infared absorption peak shape of an adsorbate layer in order to determine the existance and relative importance of all these different mechanisms. The experimental setup has been described elsewhere.[1,10] The sensitivity of the infrared spectrometer has been considerably increased, so the absorption peak has been determined by integrating the first-derivative spectrum, recorded with a modulation amplitude of $\frac{1}{10}$ the slit width, the latter being 1.4 cm^{-1}. With this small modulation, our infrared spectrometer records the first derivative of the absorption with an error of about 5%.[11] The presented data are unsmoothed, and after subtraction of the measured background the baseline was absolutely flat.

In Fig. 1 we show the integrated infrared absorption peak of an ordered $c(2\times2)$ structure compared with a Lorentzian and a Gaussian distribution. It is evident that the absorption peak has a predominantly Lorentzian shape, indicating that *the inhomogeneous broadening,* caused by different kinds of disorder in the adsorbate layer, *is very small.* There is some tailing towards higher frequencies which we discuss later.

In Table I we compare the linewidth of the ordered $c(2\times2)$CO/Cu(100) structure at 20 and 130 K. There is no detectable temperature dependence, showing that *phase relaxation is negligible.* Despite this, a strong temperature dependence has been observed for the *bridge-bonded* CO molecules on Ni(111), the width being from 6–20 cm^{-1} in the 50–300 K range.[5,6] We have, in a recent work,[6] shown

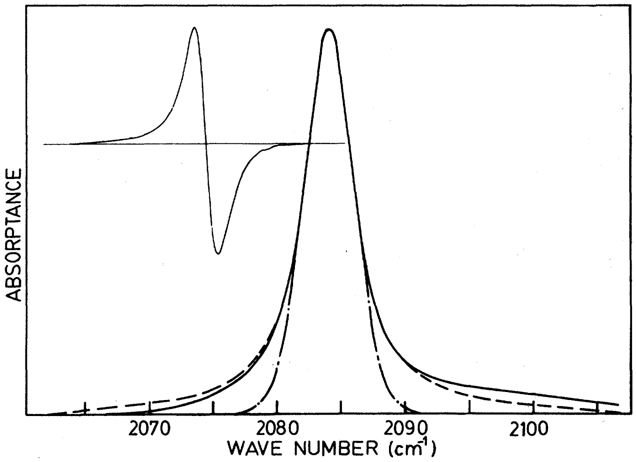

FIG. 1. The integrated infrared absorption peak (——) of the ordered $c(2\times2)$ structure (coverage 0.5) of CO on Cu(100) at 100 K. Spectrometer resolution, 1.4 cm^{-1}. Lorentzian (— — —) and Gaussian (— · — ·) distributions are shown. The recorded first-derivative spectrum is given in the inset.

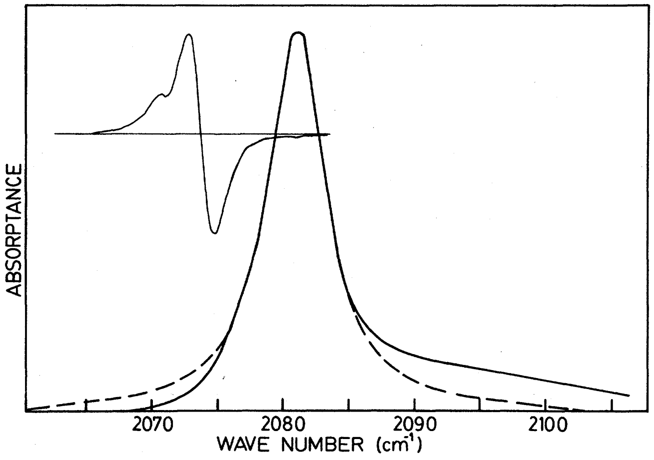

FIG. 2. The integrated infrared absorption peak (——) of an incomplete monolayer (coverage 0.35) of CO on Cu(100) at 100 K. A Lorentzian distribution (— — —) is also shown.

that this is caused by anharmonic coupling to a specific low-frequency mode, a hindered rotation. The strength of the dephasing process depends critically on the energy of the low-frequency mode, the damping rate of this mode, and the coupling strength. Appropriate values of these parameters for *on-top* bonded molecules indicated that the phase relaxation should be much weaker than for the bridge-bonded ones. The present data show, in fact, that for the on-top bonded molecules in the $c(2\times2)$/Cu(100) structure the effect of dephasing is absolutely negligible. The obvious conclusion is, therefore, that for the $c(2\times2)$ structure *the peak width is a true measure of the vibrational damping rate.*

In Fig. 2 we show the spectrum for an incomplete layer, with a coverage of 0.35. The width has increased by 0.7 cm^{-1} (Table I) and the peak has lost much of its Lorentzian shape; the high-frequency tail is now much more pronounced. Let us therefore consider the peak shapes in more detail. The straightforward interpretation is, of course, that the asymmetry and increased width is caused by inhomogeneous broadening. As mentioned above, the long-range dipole-dipole interaction gives rise to an additional broadening for an incomplete layer, but only for *low* coverages and with a low-frequency tail.[2] However, for CO on Cu there exists a counteracting coverage-dependent "chemical" shift of nearly the same magnitude[1] (compare Fig. 4 in Ref. 12). The "chemical" shift can be composed by several parts but it will certainly have a strong short-range component. One would therefore expect high coverage inhomogenieties to produce spectra like in Fig. 2 together with some additional broadening. The most likely interpretation of the small deviation from a pure Lorentzian in Fig. 1 is then that it is a measure of the perfection of the $c(2\times2)$ structure, but effects caused by such processes as mentioned above cannot be excluded.

Gadzuk and Luntz[3] have pointed out that the interaction between a vibrational mode and the deexcitation continuum of electron-hole pairs will, if the peak broadening is caused by energy relaxation, produce a high-frequency tail. The question is how pronounced the asymmetry would be and the presented theory does not make it possible to determine the strength of the effect. Langreth[9] proposed very recently a peak asymmetry caused by nonadiabatic effects. A high-frequency tail implies, as he also points out, that the increase in the dynamical dipole moment μ caused by chemisorption has an opposite sign compared to that of free CO. This would be in contradiction to a recent cluster calculation,[13] which indicates an increase in μ by 0.1 D in the same direction as that of free CO (quite in line with the experimental value[2]). More important, both models consider an

TABLE I. The vibrational frequencies and intrinsic linewidths (FWHM) of the C–O stretch mode of different configurations of CO. The spectrometer bandwidth has been subtracted.

	Coverage		Temp. (K)	Vibrational frequency (cm^{-1})	Width (cm^{-1})
Cu(100)	0.50	$c(2\times2)$	130	2084 ± 2	4.6 ± 0.5
	0.50	$c(2\times2)$	20	2086	4.6
	0.35	incomplete	100	2081	5.3
Ni(111)	0.50	$c(4\times2)$	30	1898	6 ± 1

isolated chemisorbed molecule and do not include the lateral interaction in an adsorbate layer. In general, these give rise to considerable frequency redistribution, such as the strong intensity transfer to high-frequency modes caused by the dipole-dipole interaction.[2] Therefore, the validity of the theories above for the present case of an ordered layer seems rather limited.

The final test of the broadening mechanism for this chemisorption system would have been to measure the isotope effect on the linewidth. For the electron-hole pair mechanism the lifetime is proportional to the reduced mass,[3,7] so a comparison for the $c(2\times2)$ structure between $^{12}C^{16}O$ and $^{13}C^{18}O$ would give a difference of 0.3 cm^{-1}, quite measurable with the present resolution. However, to our knowledge it is not possible to purchase $^{13}C^{18}O$ with an isotopic purity better than 90%. Because of the strong dipole-dipole interaction, isotopic impurities give rise to an additional broadening[2] of the order of 1 cm^{-1}, which effectively masks any isotope effect. To avoid this we tried to study very dilute systems down to coverages of $\frac{1}{50}$ monolayer, but this was not dilute enough and we still detected some additional broadening.

In Table I the width of bridge-bonded CO molecules in the $c(4\times2)$ structure on Ni(111) is also given.[6] The value is much smaller than what has previously been assumed for transition metals and only 30% larger than on copper.

If the vibrational damping rate is caused by charge oscillations between a $2\pi^*$ resonance and the metal, then this process gives also the main contribution to the *increase* in dynamical dipole moment μ that is observed. Despite the increase in binding energy by a factor of 2 on Ni compared to Cu, it turns out that μ is almost the same.[14] Including the electronic screening[2] (with $\alpha_e = 3.0$ Å^3), we obtain $\mu = 0.21$ D for $c(4\times2)$/Ni(111) compared to $\mu = 0.25$ D for $c(2\times2)$/Cu(100). It is not feasible to transform these values into magnitudes of oscillating charge, because the image plane of Ni is poorly defined and the exact position of the bridge-bonded molecules is not known. Suffice to say that the relative values of μ and Δ are consistent. It also indicates that the strengthening of the chemisorption bond mainly goes via the 5σ orbital, which contributes rather little to the dynamical dipole moment.[13]

Finally, it is satisfying to find that the values for CO on Cu(100) in Table I agree well with our previous work,[1] where we used two other methods to determine the intrinsic linewidth. Less satisfying is to report that the widths of the C–H stretch modes of chemisorbed CH_3O, which we in a previous paper[15] regarded as a measure of the damping, has been shown to be caused by inhomogeneous broadening.[16]

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