

Vibrational phase relaxation of the metal-molecule stretch mode: CO on Pt(111)

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(Received 5 May 1989)

The metal-molecule stretch vibrational mode of CO chemisorbed on a Pt(111) surface has been studied by infrared spectroscopy. The spectra for the on-top bonded molecules in the $c(4\times 2)$ structure show a strong temperature dependence, which is shown to be caused by an anharmonic coupling to the frustrated translation and an order-disorder transition. A theory previously developed for the phase relaxation of high-frequency intramolecular modes is shown to describe equally well the dephasing of this low-frequency metal-molecule mode.

Infrared spectroscopy of adsorbed molecules has been developed into a very powerful surface-science tool during the last decade. Owing to the inherent high resolution of the spectroscopy, much fundamental information has been obtained about the properties of the high-frequency, intramolecular vibrational modes. From studies of the shape and width of the infrared absorption peak, today we have a good understanding of the interaction between these modes and other excitations in the adsorption system. The interaction with the substrate can give rise to a strong damping of the vibrational mode, there can be a substantial intermolecular interaction between the adsorbed molecules, and the coupling to thermally excited, low-frequency modes can give rise to a vibrational phase relaxation, as thoroughly discussed in a recent paper.¹

However, it has been a remaining experimental challenge to expand the energy range of the spectroscopy below 500 cm^{-1} while maintaining enough sensitivity to detect the weak substrate-adsorbate modes of chemisorbed molecules or atoms. The properties of these modes are extremely important for all dynamical surface processes, as they are the vibrational levels in the substrate-adsorbate binding potential. In processes like adsorption, desorption, and surface reactions they will often be highly excited and the interaction between these modes and other excitations will therefore be very important for the dynamical properties of the system. It would also be interesting to find out if the concepts and theories developed for the high-frequency modes also hold for these low-frequency vibrations. In this Rapid Communication I report the first study on the phase relaxation of a metal-molecule mode, namely the Pt-CO stretch vibration.

The technical problem in designing a reflection spectrometer for the low-frequency region is not a question of finding new light sources, better detectors, or even new optical schemes, but to obtain maximum stability in the whole experimental setup.² The reason is that in an optical experiment like this, one is always, in one way or another, looking for a small difference between two large signals, in this case with and without molecules adsorbed on the surface. I have, therefore, in several stages improved on my infrared spectrometer along this line, and have finally succeeded in obtaining the necessary sensitivity to detect the metal-molecule stretch mode of CO on

Pt(111). The spectrometer has been described elsewhere.^{1,3} In brief, it is a dispersive vacuum spectrometer using the wavelength modulation technique. The signal at the fundamental modulation frequency was recorded, which is mainly proportional to the first derivative of the absorbance. To minimize background variation and surface contamination, a sequence of reference, and adsorbate spectra was taken, each spectrum being measured for only 20 min. Consecutive difference spectra were constructed and six such difference spectra, corresponding to four reference and three adsorbate spectra, were then added and numerically integrated. It turned out that the width of the infrared absorption peak was very sensitive to inhomogeneities in the adsorbate layer, but the following cleaning procedures finally gave reproducible results. The crystal was oriented within 0.3° and mechanically polished down to a $0.25\text{-}\mu\text{m}$ diamond paste. The *in situ* cleaning consisted of numerous cycles of annealing in vacuum at 1150 K, oxidation (10^{-6} torr O_2) at 1000 K, and low-energy sputtering (Ar^+ , 250 eV, $1\text{ }\mu\text{A}/\text{cm}^2$) at room temperature. During these procedures the surface kept its mirrorlike finish.

Some years ago, Tobin and Richards⁴ were able to detect the metal-molecule vibrational mode of CO on Pt(111) using infrared emission spectroscopy. They reported for the Pt-CO mode a width of about 8 cm^{-1} at 200 K but were, due to a large spread in the data, unable to establish any temperature dependence. Recently, Hoge *et al.*⁵ published a study on the metal-molecule mode for the same CO-Pt(111) system, using an infrared Fourier-transform spectrometer. They reported a peak width of $4\text{--}5\text{ cm}^{-1}$ and with almost no temperature dependence in the 100–300 K range. They suggested that the width was caused by vibrational damping due to excitations of electron-hole pairs in the metal and that the influence from any anharmonic coupling to other modes was negligible. Very recently, Malik and Trenary⁶ completed a similar study on the same system, using the same technique. They found a width of about 3 cm^{-1} at 80 K, which increased to 8 cm^{-1} at 300 K. This temperature dependence is attributed to vibrational damping via three-phonon excitations.

However, in this paper I will demonstrate that most of the previous results were severely affected by inhomogeneous broadening, which masked important information

about this chemisorption system. By a careful cleaning and adsorption technique it was possible to obtain reproducible results for the infrared absorption-peak position and width. Figure 1 shows infrared absorption spectra of the Pt-CO mode of the on-top bonded molecules in the $c(4 \times 2)$ structure of CO on Pt(111) in the temperature range 100–300 K. The spectra were recorded in the way described above and exhibit a minor frequency shift but a rather strong temperature dependence of the width. This is explicitly shown in Fig. 2, where the peak position and the full width at half maximum (FWHM) are plotted as a function of temperature. The spectrometer resolution of 2.6 cm^{-1} is subtracted, assuming Gaussian distributions, i.e., that the widths add quadratically. We find a small decrease in vibration frequency, from 462 cm^{-1} at 100 K to 460 cm^{-1} at 290 K. The width shows a linear increase from 2.5 cm^{-1} at 100 K to 4.1 cm^{-1} at 250 K, then with an increased slope up to 5.9 cm^{-1} at 290 K. Obviously, we observed the effect of two peak-broadening processes, where one is in operation from 100 K and upwards, while another is setting in at 250 K.

When discussing processes affecting the width of the infrared absorption peak, we have, in analogy with the work on the high-frequency intramolecular modes, to consider three major peak-broadening mechanisms,¹ i.e., inhomogeneous broadening, phase relaxation, and vibrational damping. Inhomogeneities in the adsorbate layer will give rise to a broadening of the infrared absorption peak because the molecules will have different local environments, giving them slightly different vibration frequencies. This broadening was definitely dominating the widths observed in previous work.^{4,5} I have also shown in another paper how this sensitivity to inhomogeneities of the Pt-CO mode can be used to study phase transitions in the overlayer.⁷

Inhomogeneous broadening is generally expected to

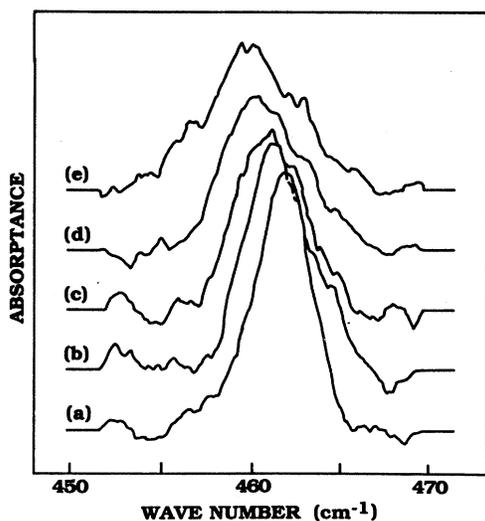


FIG. 1. Infrared absorption spectra of the Pt-CO stretch vibrational mode of the on-top bonded molecules in the $c(4 \times 2)$ structure of CO on Pt(111) at (a) 100 K; (b) 185 K; (c) 225 K; (d) 260 K; and (e) 290 K. The ends of each spectrum indicate the chosen baseline.

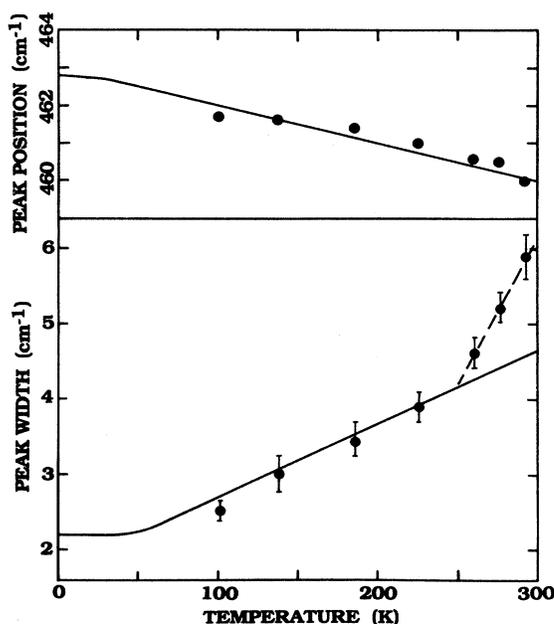


FIG. 2. The position and width (FWHM) of the infrared absorption peak of the Pt-CO stretch vibrational mode of the on-top bonded molecules in the $c(4 \times 2)$ structure of CO on Pt(111) as a function of temperature. The solid lines are calculated using a theory for the anharmonic coupling to the frustrated translation.

show a weak temperature dependence, provided there is no thermally induced disorder in the overlayer. However, that is actually what happens above 250 K, where we find the extra contribution to the width in Fig. 2. Schweizer *et al.*⁸ have made a recent infrared investigation of the internal C-O stretch mode for this system, combined with low-energy electron diffraction (LEED) intensity measurements. They found an order-disorder transition, starting at 250 K and saw it as both a decrease in LEED intensity of a $(0, \frac{1}{2})$ spot and an increase in the peak width of the bridge-bonded molecules in the $c(4 \times 2)$ structure. Obviously, this phase transition is also seen in the width of the Pt-CO mode of the on-top bonded molecules in Fig. 2. Below 250 K the LEED intensity only follows an expected Debye-Waller law,⁸ so the thermally induced inhomogeneous broadening in this temperature region should be negligible.

By the interaction with the substrate, a vibrational excitation will have a finite lifetime, which due to the uncertainty principle will give rise to a broadening of the infrared absorption peak. It seems clear that this vibrational damping gives the absorption peak of the internal C-O mode an intrinsic width of about 5 cm^{-1} , as a consequence of the particular electronic structure of chemisorbed CO.¹ The vibrational damping of the Pt-CO mode is discussed in detail elsewhere,⁹ where it is shown that the homogeneous broadening is less than 1 cm^{-1} and caused by electron-hole pair excitation, which is rather temperature independent. Even if it is possible to relate the temperature dependence of the peak width seen in Fig. 2 to vibrational damping via three-phonon creation, as

was done by Malik and Trenary,⁶ a new theoretical calculation on this process shows that the peak broadening from this mechanism is orders of magnitude smaller.¹⁰

Therefore, it is quite possible that the dominating part of the increase in width with increasing temperature, which is seen from 100 K and upwards in Fig. 2, is caused by phase relaxation, i.e., the anharmonic coupling to thermally excited, low-frequency modes. The effect on the peak width from the anharmonic coupling to the *substrate phonons* has been discussed by Persson¹¹ and Zhang and Langreth¹² for CO on Ni and they estimated the broadening to be of the order of 1 cm^{-1} at 300 K. However, the new theoretical calculation mentioned above shows that the previous calculations exaggerate the contribution to the linewidth from the phonon interactions by orders of magnitude because of a missing factor.¹⁰

We have previously developed a theory that accounts very well for the phase relaxation of the internal C-O stretch mode of CO-Ni(111) and CO-Ru(001) (Ref. 13), which has also been successfully applied on CO-Pt(111).⁸ It considers the anharmonic coupling to one thermally excited *normal mode* of the chemisorbed molecule and the phase relaxation is described by three parameters: the frequency ω_0 of the low-frequency mode, the damping rate η of this mode, and the coupling strength $\delta\omega$ (more exactly, the frequency shift of the studied mode when the thermally excited mode goes from its ground state to its first excited state). The only normal mode that can have a reasonable population at temperatures below 300 K is the frustrated translation. This mode consists of mainly translational but also some rotational motion centered at the binding (in this case on top) position. As the Pt-CO mode has different vibration frequencies in the on-top (460 cm^{-1}) and bridge [380 cm^{-1} (Ref. 14)] position, a motion away from the on-top position will decrease the frequency. A harmonic translational motion around the on-top position may then produce a broadening of the peak. The interesting question is now to what extent this model, which seems to work well for the high-frequency internal C-O mode, also holds for the low-frequency Pt-CO mode. The frustrated translation has been studied by He scattering¹⁵ and found to have an energy of $\omega_0 = 60 \text{ cm}^{-1}$ for the on-top bonded CO molecules in the $c(4 \times 2)$ structure on Pt(111). The width of the inelastic scatter-

ing peak is smaller than 20 cm^{-1} (Ref. 15) (possibly below 8 cm^{-1}), which sets an upper limit to η . In previous work on the phase relaxation of the internal C-O mode, it was not possible to estimate $\delta\omega$. For the metal-molecule stretch mode the situation is more favorable and one can rather accurately estimate $\delta\omega$ to $\sim -1 \text{ cm}^{-1}$.¹⁰

The solid lines in Fig. 2 are calculated¹⁰ using the theory of the vibrational phase relaxation previously discussed above¹³ using the following parameter values:

$$\omega_0 = 60 \text{ cm}^{-1}, \quad \delta\omega = -1.2 \text{ cm}^{-1}, \quad \text{and} \quad \eta = 6 \text{ cm}^{-1}.$$

These values fit very well into the discussion above. Obviously, the picture that we have developed for the vibrational phase relaxation of a high-frequency internal mode holds equally well for the low-frequency metal-molecule mode. This result is also an independent proof that this theory describes the dephasing process very well and that the parameter values produced by the theory are related to relevant physical quantities.

At very low temperatures the effect of the phase relaxation vanishes, as the frustrated translation is no longer excited. We are then left with a temperature-independent contribution to the width of about 2 cm^{-1} . In the work on the internal C-O mode^{8,13} this contribution was about 5 cm^{-1} and was associated with the homogeneous broadening due to the vibrational damping. However, as mentioned above, I have shown elsewhere⁹ that for the Pt-CO mode the homogeneous broadening is less than 1 cm^{-1} , so this constant contribution must be due to a temperature-independent inhomogeneous broadening, caused by structural disorder.

To conclude, this work has shown that for the on-top bonded CO molecules on the Pt(111) surface the Pt-CO vibrational mode exhibits an anharmonic coupling to the frustrated translation. The vibrational phase relaxation is very well described by a theory previously developed for the internal C-O mode. A thermally induced order-disorder transition in the $c(4 \times 2)$ structure is also clearly observable in the temperature dependence of the infrared absorption-peak width.

I thank Bo Persson for performing the calculation and for constructive comments and Stig Andersson for numerous encouraging discussions.

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