

Phase transitions in a chemisorbed overlayer studied by infrared spectroscopy: CO on Pt(111)

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Infrared spectroscopy of the metal-molecule stretch vibrational mode has been used to study phase transitions in an overlayer of CO on a Pt(111) surface. The width of the infrared absorption peak is used as a measure of the ordering in the overlayer and shows a very strong variation, as function of both coverage and temperature. Coupled to low-energy electron-diffraction studies, the variations are found to be caused by order-disorder transitions. By use of different CO isotopes, important information is obtained about the intermolecular interaction responsible for the peak broadening and probably also for the ordering in the overlayer.

One of the goals of surface science is to understand the forces responsible for surface ordering. Two-dimensional phase transitions have been studied both experimentally and theoretically for several years.¹ A class of systems of particular interest is the order-disorder transitions in layers of atoms or molecules adsorbed on a surface. Generally, these transitions are a function of both adsorbate density and temperature. Often the experimental approach has been to use some kind of scattering technique, such as He scattering² or most commonly low-energy electron diffraction (LEED).³ Even if it is possible to construct the phase diagram of a chemisorption system using such methods, they are best suited to study the temperature dependence at a fixed coverage. The interpretation of the LEED intensities is far from straightforward,⁴ relying heavily on theoretical calculations. In this Rapid Communication I present a new method for investigating phase transitions in an adsorbate layer, namely, infrared spectroscopy. More specifically, the width of the infrared absorption peak of the low-frequency metal-molecule stretch vibrational mode is used as a measure of the order in the overlayer, as both the adsorbate coverage and the substrate temperature is varied. The investigated system is CO chemisorbed on a Pt(111) surface. The experimental conditions will be described in detail elsewhere.⁵

Due to the inherent high resolution of infrared spectroscopy, much fundamental information has been obtained about the properties of high-frequency, intramolecular vibrational modes by studies on the shape and width of the infrared absorption peak, as is thoroughly discussed in a recent review paper.⁶ However, it has been a remaining experimental challenge to expand the energy range of the spectroscopy below 500 cm^{-1} , with enough sensitivity to detect the weak substrate-adsorbate modes of chemisorbed molecules or atoms. Some years ago, Tobin and Richards were able to detect the metal-molecule stretch mode of CO on Pt(111) (Ref. 7) using infrared emission spectroscopy. They reported for this mode a peak width of about 8 cm^{-1} at 200 K, but were unable to establish any coverage or temperature dependence due to a very large scatter in the data. Recently, Hoge *et al.*⁸ 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 $4\text{--}5\text{ cm}^{-1}$ with only a minor coverage and temperature dependence. Very recently, Malik and Trenary⁹ have made a similar study on the same system and using the same technique. They found a constant width of about 3 cm^{-1} at low coverages, which increases rapidly to 6 cm^{-1} for coverages above 0.3. The temperature dependence is reported to follow a T^2 law.

However, since CO on Pt(111) shows a number of order-disorder transitions both with respect to coverage and temperature, one would expect that this should show up more clearly in the infrared spectra, especially in the peak width. In this Rapid Communication I will demonstrate that these transitions give rise to dramatic effects, which are critically sensitive to the specimen cleaning and adsorption technique and that the previous results were severely affected by inhomogeneous broadening, which masked important information. The width has, in general, three contributions. Because of the uncertainty relation, the finite lifetime of the vibrational excitation gives rise to a lifetime broadening (damping), there can be an anharmonic coupling to other, thermally excited low-frequency modes (dephasing) and there can be an inhomogeneous broadening caused by disorder in the overlayer.⁶ The effects of the two former processes on the Pt-CO stretch mode will be discussed elsewhere.⁵

The origin of the inhomogeneous broadening is that in a disordered system the molecules have different surroundings, which give them slightly different vibration frequencies. I will show, that if the influence from surface defects and contamination is minimized, the inhomogeneous broadening can be used as a measure of the order in the overlayer. Even if the frequency shift of an individual molecule is a local effect, the total width of the infrared absorption peak measured coherently over distances of the order of the wavelength ($20\text{ }\mu\text{m}$), is a collective property. Figure 1 shows the full width at half maximum (FWHM) and position of the infrared absorption peak of the Pt-CO stretch vibrational mode for the on-top bonded molecules as a function of coverage at 100 K. The spectrometer resolution of 2.6 cm^{-1} is subtracted, assuming Gaussian distributions (that the widths add quadratically). Doses have been converted to coverage using the sticking

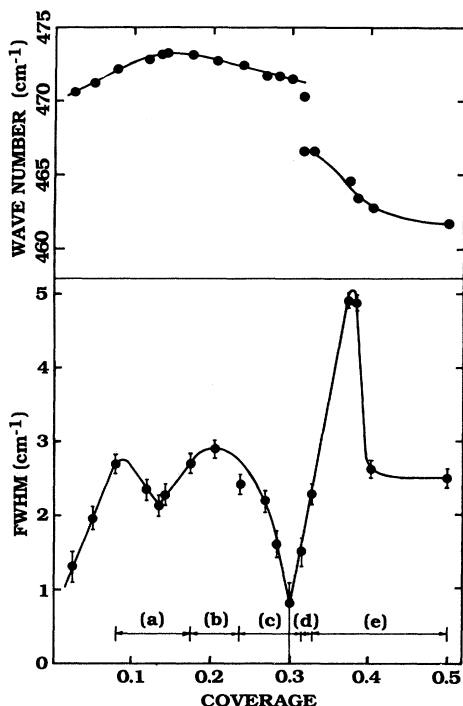


FIG. 1. The width (FWHM) and position of the infrared absorption peak of the on-top bonded molecules of CO on Pt(111) at 100 K as a function of CO coverage. Indicated is also the observed LEED patterns as (a) (4×4) , (b) diffuse $(\sqrt{3} \times \sqrt{3}) \times R30^\circ$, (c) (8×8) , (d) $(8 \times 8) + c(4 \times 2)$, and (e) $c(4 \times 2)$.

coefficient reported by Steininger, Lewald, and Ibach¹⁰ [assuming $\Theta = 0.30$ for the (8×8) structure]. The surprisingly strong and sharp variation of the width with coverage indicates that the width is dominated by inhomogeneous broadening caused by structural disorder in the overlayer, as the effects of surface defects and contamination, as well as vibrational damping and dephasing, are expected to be rather independent of the CO coverage. Such a strong coverage dependence of the width, as is shown in Fig. 1, has not been previously reported. The main reason is that a vibrational mode that is so sensitive to structural disorder, is equally sensitive to other kinds of inhomogeneities, which may then dominate and mask the effect, as in previously reported works.⁷⁻⁹

The CO/Pt(111) system exhibits three ordered, un-compressed structures at low temperatures.¹⁰ The $c(4 \times 2)$ structure corresponds to a coverage (with respect to the number of surface Pt atoms) $\Theta = 0.5$, with half of the molecules in the on-top position and half of them bridge bonded. For the two low-coverage structures Tüshaus *et al.*¹¹ have proposed real-space models, denoted (4×4) and (8×8) , with all molecules in the on-top position and $\Theta = 0.19$ and 0.30 , respectively. In Fig. 1 the sequence of observed LEED patterns is indicated and from this, it is obvious that the minima in the width is connected with the ordering in the overlayer. Starting with the (8×8) structure at $\Theta = 0.30$, the data show a very sharp order-disorder transition for this structure. The width for

the ordered structure is below 1 cm^{-1} , accompanied with a sharp (8×8) LEED pattern. The very small width at this coverage also shows that the overall contribution to the width from surface imperfections is small.

The ordering of the (4×4) structure has the same discontinuous character, but shows a fairly large residual inhomogeneous width. This indicates that it is not possible to obtain a well-ordered (4×4) structure, which was confirmed by the LEED pattern showing rather diffuse spots. Measurements at 60 K for this coverage showed a decrease in width to 1.6 cm^{-1} , but with no improvement of the LEED pattern. The minimum in the width occurs at $\Theta = 0.13$, which is considerably less than $\Theta = 0.19$ of the suggested real-space structure.¹¹ Either this deviation originates from the fact that the structure is never fully developed, or the proposed structure is not correct.

When the coverage is increased above $\Theta = 0.30$, a good $c(4 \times 2)$ LEED pattern develops already at $\Theta = 0.33$. The overlayer must turn into a very disordered state with $c(4 \times 2)$ islands in a disordered matrix. This is seen in the very large increase of the peak width, which then gradually decreases when the overlayer develops an increasingly homogeneous $c(4 \times 2)$ structure. The transition has, of course, a continuous character. This tendency to easily form $c(4 \times 2)$ islands explains why the high symmetry $(\sqrt{3} \times \sqrt{3})R30^\circ$ with $\Theta = 0.33$ is never obtained, while the proposed (4×4) and (8×8) structures have a $(\sqrt{3} \times \sqrt{3})R30^\circ$ basis.¹¹ The nature of the intermolecular interaction, or rather the interplay between different interactions, responsible for such a behavior must be very delicate.

The $(8 \times 8) - c(4 \times 2)$ transition is also seen in the peak position in Fig. 1. The coexistence of two peaks at $\Theta = 0.32$ shows that there is no continuous transition of the vibration frequency, but that the two different modes belong to two different situations. The mode with a vibration frequency above 470 cm^{-1} is associated with molecules having only on-top bonded neighbors, while the mode around 465 cm^{-1} is connected to the on-top bonded molecules in or close to a $c(4 \times 2)$ island.

Having explored the coverage dependence of the order in the overlayer, it would be interesting to also study the temperature effects. Figure 2 shows the peak width as a function of substrate temperature for $\Theta = 0.28$ and the $c(4 \times 2)$ structure. For $\Theta = 0.28$, the increase in width with temperature is very strong, accompanied with the LEED pattern getting more and more diffuse, being very blurred at 150 K. From the plot we find that even at 100 K, there is a substantial thermally induced broadening.

For the $c(4 \times 2)$ structure the picture is more complicated, as we observe two temperature-dependent contributions to the width, one operating over the whole measured temperature range and one setting in at 250 K. However, Schweizer *et al.*¹² have made a recent infrared investigation of the internal C-O stretch mode for the CO/Pt(111) system, combined with LEED intensity measurements. They find an order-disorder transition, starting at 250 K, and see both as 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, the rapid increase in width above 250 K that is seen in Fig. 2,

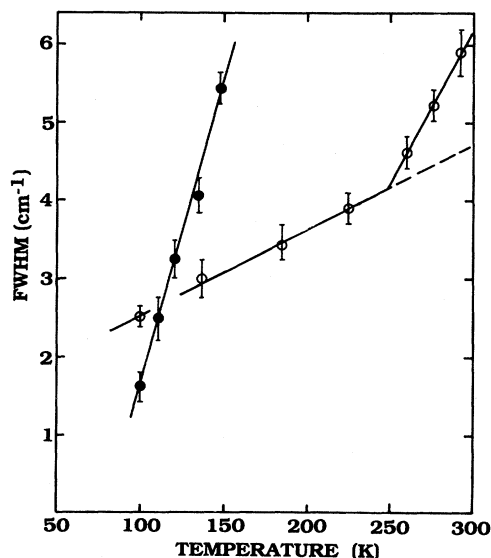


FIG. 2. The width (FWHM) of the on-top bonded molecules of CO on Pt(111) for $\Theta=0.28$ and in the $c(4 \times 2)$ structure (open circles) as a function of temperature.

is associated with this thermally induced order-disorder transition.

Another fundamental question raised by this work concerns the nature of the molecule-molecule interaction that gives rise to the inhomogeneous broadening. If there were no such interaction, the molecules would, of course, act as independent oscillators and none of the effects discussed above would be observed. It is not too speculative to assume that this interaction also plays an important role in the ordering of the whole system, as the peak broadening reflects changes in the shape of the CO-Pt binding potential. In general, we may divide the possible kinds of interactions into long or short ranged, direct or indirect, static or dynamic.⁶ The long-range interaction goes via the dipole fields of the molecules. The static dipole moment for CO on Pt(111) is rather small, as is seen in the change in work function, being -0.4 eV at $\Theta=0.2$, 0 at $\Theta=0.4$, and $+0.15$ eV at $\Theta=0.5$. The dynamical dipole moment of the metal-molecule stretch mode is about 1 order of magnitude smaller than for the internal C-O stretch mode,⁶ which would also make the dynamical dipole-dipole interaction negligible.

The direct short-range interaction, which is due to the overlap of the molecular orbitals, sets in at molecule-molecule distance below 3 \AA and is ruled out for $\Theta \leq 0.5$, but may be important for higher coverages, where the nearest-neighbor positions are occupied.

The indirect, short-range interaction can either go via the substrate lattice or the conduction electrons. The former dynamical interaction is caused by the anharmonic coupling between the metal-molecule stretch mode and the metal phonons. The latter interaction is caused by the electronic screening of the chemisorbed molecule and may have both a static and a dynamical contribution.

To exclude some of these interactions which might be responsible for the peak broadening, the width as a func-

tion of the molecular mass was recorded at different coverages. The results are shown in Fig. 3 as the width versus the vibration frequency for the $^{12}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$, and $^{13}\text{C}^{18}\text{O}$ isotopes at three coverages: $\Theta=0.1$, $\Theta=0.2$, and $\Theta=0.5$. Consider first the coverages below 0.30, with all molecules in the on-top position. First of all, the data in Fig. 3 clearly indicate that the interaction has a dynamic character, as the width decreases with increasing mass. There is no reason to expect any explicit frequency dependence of the interaction, but for a harmonic motion both the frequency and the *amplitude* are proportional to $(M^{-1})^{1/2}$. A decrease in amplitude weakens the strength of the interaction and hence gives a smaller broadening, as seen in the figure. This suggests that at least part of the inhomogeneous broadening is due to a short-range, dynamic interaction, caused by the coupling between the metal-molecule stretch vibrational mode and the substrate. Whether the interaction is an electronic coupling or occurs via substrate phonons is very difficult to determine experimentally, as the temperature dependence that the latter should exhibit is hard to separate from thermally induced disorder in the overlayer, as seen in Fig. 2, or from the effects of dephasing.⁵

If we consider the ordered $c(4 \times 2)$ structure, the situation is quite different. We find nearly no isotopic dependence, even if the scatter of the data points is a bit larger. This indicates that the inhomogeneous broadening is of a static origin, which gives as the only possibility a short-range coupling via the conduction electrons.

It is not easy to correlate the experimental results above with the vast amount of existing theoretical work on two-dimensional phase transitions in chemisorption systems.^{4,13} Most works have considered the critical exponents and universality classes of second-order transitions, which depends on the symmetry of the adsorbate system, but little has been done on the direct nature of the molecule-molecule and the molecule-substrate interactions, which are responsible for the properties studied in this work. However, Persson¹⁴ has recently taken a new approach by carrying out a Monte Carlo simulation using a realistic potential-energy surface constructed from infrared studies of the high-frequency C-O stretch mode of CO/Pt(111).¹⁴ He is able to reproduce the structures

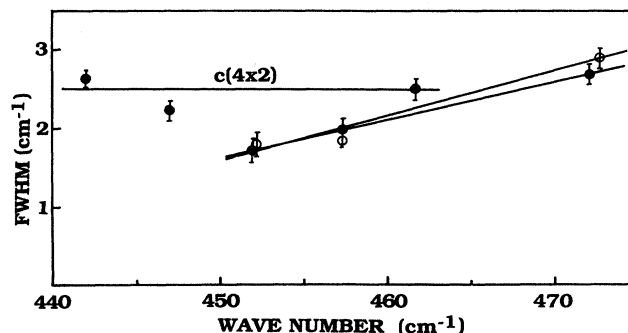


FIG. 3. The width (FWHM) of the on-top bonded molecules of CO on Pt(111) for $\Theta=0.1$, $\Theta=0.2$ (open circles) and in the $c(4 \times 2)$ structure for the $^{12}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$, and $^{13}\text{C}^{18}\text{O}$ isotopes measured at 100 K.

with $\Theta \geq 0.5$, but not the (4×4) and (8×8) structures with their larger unit cells. Still this seems to be a fruitful approach if a realistic model for the molecule-molecule interaction can be constructed. Calculations of the peak width for all coverages and comparison with data, such as those in Fig. 1, would then provide a much better test on models of these interactions, than just obtaining the correct ordered structures.

In conclusion, I have shown how infrared spectroscopy of the metal-molecule mode can be used as a powerful tool

to investigate phase transitions in adsorbate overlayers. Studies on the isotopic dependence of the width give new, important information about the intermolecular interaction that may play an important role for the ordering of the structures.

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