RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 44, NUMBER 23 15 DECEMBER 1991-I

Vibrational study of a combination band and the effects of inhomogeneous broadening: CO on Pt(111)

R. Ryberg

Physics Department, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

(Received 6 May 1991)

The combination band of the Pt-CO and the C-O stretch vibrational modes of carbon monoxide chemisorbed on a Pt(111) surface has been studied by infrared spectroscopy. The width of this combination band is much larger than the sum of that of the two fundamental modes. By studies of the width of the C-O stretch mode in the dilution limit of isotopic mixtures, it is found that the effects from surface imperfections are negligible. This indicates that the large width of the combination band at low temperatures is caused by the dispersion of the C-O stretch mode and at high temperatures by inhomogeneous broadening.

It is common knowledge that a free molecule has $3N$ degrees of freedom, so a diatomic molecule like carbon monoxide has three translational, two rotational, and the internal C-O stretch vibrational modes. When the molecule is chemisorbed on a metal surface the number of modes is preserved, but the presence of the surface put certain restrictions on the modes and one gets two frustrated lateral translations and two frustrated rotations (for certain sites degenerated), the frustrated translation normal to the surface, which we call the metal-CO stretch vibration and the C-O stretch mode.[1] Quite naturally, nearly all spectroscopic work has dealt with these fundamental modes. However, it is also possible to excite two of these fundamentals simultaneously (either via the anharmonic coupling between the modes or nonlinear terms of the dynamical dipole moment), forming what is called a combination band. For the CO/Pt(111) chemisorption system, Lehwald, Ibach, and Steininger,[2] using electron-energy-loss spectroscopy (EELS), detected such combination bands and found that the frequencies were close to the expected sum of the fundamentals. The absorption of these combination bands is of course very weak, which has made it difficult to study them by infrared spectroscopy.

This Rapid Communication presents a detailed investigation of a combination band. It is the combination of the Pt-CO stretch vibration, which has been studied rather recently[3] and the since long well-studied internal C-O stretch mode.[4] The experimental details are given elsewhere.[3] The spectrometer resolution was 6.5 cm^{-1} at 2560 cm^{-1} and 4.4 cm^{-1} at 2100 cm^{-1}. Figure 1 shows spectra of the combination band and the two fundamental modes for the on-top bonded molecules in the $c(4\times2)$ structure of CO on a Pt(111) surface at 100 K. As the combination band has a very small dynamical dipole moment and hence gives rise to a weak infrared absorption, the spectrum was obtained in the same way as for the Pt-CO mode, i.e., as a sum of six difference spectra, each recorded for 20 min.[3] Depositions with the $^{13}\text{C}^{18}\text{O}$ isotope was made to check that the peak was not an artifact of the measuring technique. The frequency of the combination band is 2564 ± 2 cm^{-1}, which is close to the sum of the two fundamentals, about 465 cm^{-1} (Refs. 3, 5, and 6) and 2108 ± 2 cm^{-1} and also close to the value (2580 cm^{-1}) obtained by EELS.[2] The intensity is about 1:300 compared to the C-O mode uncorrected for a possible wavelength dependence of the sensitivity of the single beam infrared spectrometer [the EELS data indicate 1:100 (Ref. 2)].

The unexpected feature of the combination band is the very large width of the absorption peak, 11.4 cm^{-1}, when the spectrometer bandpass has been subtracted. One would in the first approximation expect the width of the combination band to be just the sum of that of the two fundamentals, added linearly for homogeneously and qua-

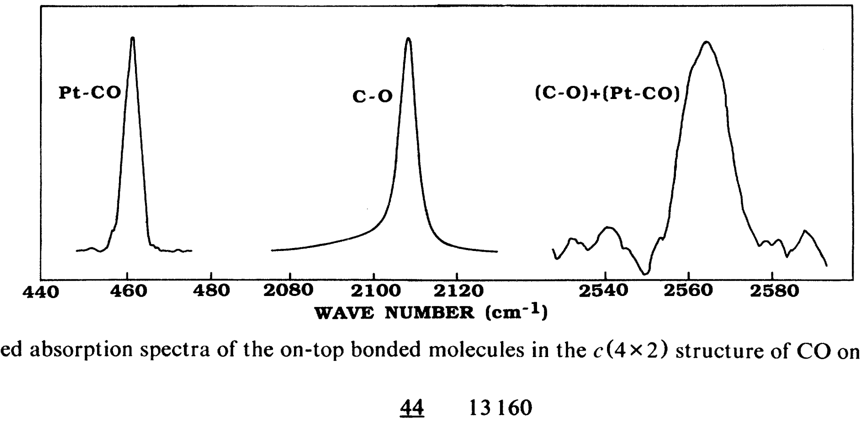

FIG. 1. Infrared absorption spectra of the on-top bonded molecules in the $c(4\times2)$ structure of CO on Pt(111) at 100 K.

dratically for inhomogeneously broadened peaks. For the CO/Pt(111) system, the Pt-CO mode has a width of 2.5 cm^{-1} (Ref. 3) and the C-O mode has a width of 3.5 cm^{-1}, so the sum of the two can at most account for half of the observed value. Since the width of the infrared absorption peak generally contains important information about the chemisorption system it is interesting to try to understand this discrepancy.

We have in a recent paper[7] discussed this problem. Following that discussion, the large width of the combination band can be caused by two different mechanisms. The requirement for an optical excitation, $\mathbf{q} \approx \mathbf{0}$, changes for the combination band to $\mathbf{q}_1 + \mathbf{q}_2 \approx \mathbf{0}$. Then the dispersion of the fundamental modes can give rise to an extra broadening. The dispersion of the Pt-CO mode is of the order of 0.1 cm^{-1}, which is negligible in this context. On the other hand, the dispersion of the C-O stretch is quite large ($\Delta\Omega = 17\ \mathrm{cm}^{-1}$) (Ref. 8) but as modes with $\mathbf{q}$ close to the zone boundary (where the dispersion is rather flat) will dominate, we estimated[7] that this effect would only account for about 2 cm^{-1} of the extra width of the combination band.

The other possibility is that the large width is caused by a strong inhomogeneous broadening of the C-O stretch mode. It was the main message of that paper that even an inhomogeneous broadening of the order of 10 cm^{-1} would not be seen in the C-O spectra due to the line narrowing caused by the dipole-dipole interaction. On the other hand, this broadening would show up for the combination band because of its small dynamical dipole moment giving a weak dipole interaction.

However, we have continued our investigation of this problem. It is in fact possible to measure the intrinsic width of the C-O stretch mode in the *absence* of the dipole-dipole interaction by using isotopic mixtures, namely by studying small concentrations of a light isotope in a matrix of a heavy one. The chemical environment is constant but at very low concentrations the light isotope will be vibrationally decoupled from the system. In Fig. 2 we show the peak width and position of the C-O stretch mode of the $^{12}\mathrm{C}^{16}\mathrm{O}$ isotope as function of concentration in a matrix of the $^{13}\mathrm{C}^{18}\mathrm{O}$ isotope. Just as above, we consider the on-top bonded molecules in the $c(4\times2)$ structure at 100 K. The mixtures were created by first depositing a small dose of $^{13}\mathrm{C}^{18}\mathrm{O}$ in order to decorate possible defects on the surface. Then the desired amount of $^{12}\mathrm{C}^{16}\mathrm{O}$ was deposited, followed by the residual amount of $^{13}\mathrm{C}^{18}\mathrm{O}$, in order to give a total dose of 5 L. Then the overlayer was annealed at 300 K and measured at 100 K. The concentrations were obtained assuming constant sticking coefficient up to $\Theta = 0.3$.[9] The isotopic purity of the $^{13}\mathrm{C}^{18}\mathrm{O}$ isotope was 98% and the spectrometer bandpass 2.9 cm^{-1}. We tested the effect of surface imperfections by omitting the first small dose of $^{13}\mathrm{C}^{18}\mathrm{O}$ and directly depositing the $^{12}\mathrm{C}^{16}\mathrm{O}$ dose, with no measurable difference.

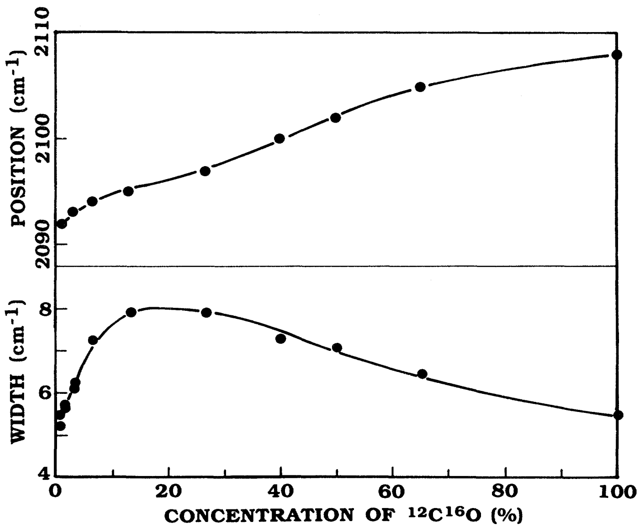

FIG. 2. The infrared absorption peak width and position of the C-O stretch mode of the $^{12}\mathrm{C}^{16}\mathrm{O}$ isotope for the on-top bonded molecules in the $c(4\times2)$ structure of $^{12}\mathrm{C}^{16}\mathrm{O}/^{13}\mathrm{C}^{18}\mathrm{O}$ mixtures on Pt(111) at 100 K as function of concentration. The spectrometer bandpass of 2.9 cm^{-1} has not been subtracted.

In a previous paper[7] we showed that due to the dipole-dipole interaction the infrared spectrum of one single isotope at high coverages will just show the homogeneous broadening, even if there exist a large amount of inhomogeneities in the overlayer. The important observation in Fig. 2 is that the width for very low concentrations is the same as for the pure $^{12}\mathrm{C}^{16}\mathrm{O}$ overlayer. Hence we can conclude that the inhomogeneous broadening due to surface imperfections is very small and can be neglected. This supports the work of Linke and Poelsma,[10] who show that a carefully prepared Pt(111) surface has a very low defect concentration.

The general behavior of the width in Fig. 2, with an increase with increasing concentration at low coverages, as this corresponds to increasing disorder for the $^{12}\mathrm{C}^{16}\mathrm{O}$ molecules, and with a decrease as the dipole-dipole interaction starts to be important, is qualitatively as predicted in earlier work on the subject.[8]

Hence we must conclude that the large width of the combination band at least at low temperatures is caused by the dispersion of the C-O mode and that we underestimated the importance of this effect in the previous paper.[7] However, the situation is somewhat more complicated. The $c(4\times2)$ structure exhibits, namely, a thermally induced order-disorder transition.[4] At low temperatures the ordered structure has half of the molecules in the on-top position and half of them bridge bonded. Increasing the temperature excites the frustrated translation, which above 250 K has such a large amplitude that the long-range order disappears. The molecules take any position between on-top and bridge,[11] and as the vibration frequency depends strongly on the adsorption site, this gives rise to a strong inhomogeneous broadening. For the disordered overlayer, $\mathbf{q}$ is no longer a good quantum number, or at least the dispersion becomes much flatter, which would make the combination band narrower.

In Fig. 3 we show the width of the combination band as function of temperature; the spectrometer bandpass has been subtracted in quadrature. In the figure is also reproduced the data for the Pt-CO mode[3] and the C-O stretch vibration. The order-disorder transition is seen very clearly as a rapid increase in the peak width, setting in at the

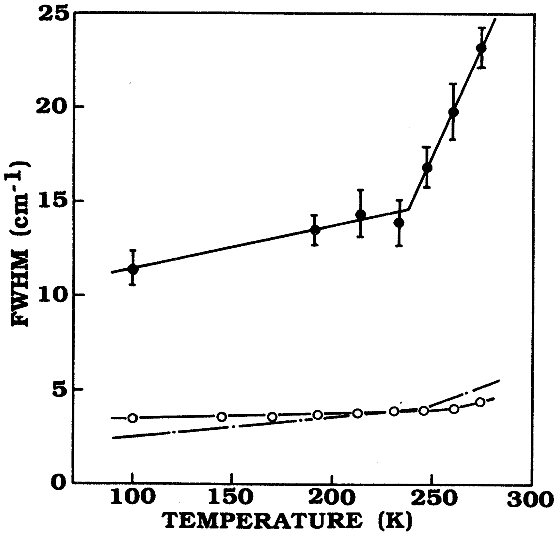

FIG. 3. The temperature dependence of the linewidth for the C-O (○), the Pt-CO (– – –), and the combination band (●). The spectrometer bandpass has been subtracted.

same temperature both for the combination and the low frequency mode and there is also a small increase in width for the C-O mode. The effect on the combination band is much stronger than on the fundamentals, which indicates clearly that at high temperatures the large width of the combination band mainly is caused by inhomogeneities in the overlayer. The large difference between the width of the combination band and the C-O mode is caused by the line narrowing due to the dipole-dipole interaction, quite in line with the discussion in the previous paper.[7]

To conclude, this study on the combination band and the isotopic mixtures in the dilution limit have shown that for our particular sample the inhomogeneous broadening of the C-O stretch mode caused by surface imperfections is negligible. The large width of the combination band at low temperatures is caused by the dispersion of the C-O mode. At higher temperatures the order-disorder transition gives rise to a very strong inhomogeneous broadening of the C-O stretch mode, which is seen very clearly in the spectra of the combination band, but for the fundamental is strongly reduced by the line narrowing due to the dipole-dipole interaction.

---

[1] N. V. Richardson and A. M. Bradshaw, Surf. Sci. **88**, 255 (1979).

[2] S. Lewald, H. Ibach, and H. Steininger, Surf. Sci. **117**, 342 (1982).

[3] R. Ryberg, J. Electron Spectrosc. Relat. Phenom. **54/55**, 65 (1990).

[4] E. Schweizer, B. N. J. Persson, M. Tüshaus, D. Hoge, and A. M. Bradshaw, Surf. Sci. **213**, 49 (1989), and references therein.

[5] D. Hoge, M. Tüshaus, E. Schweizer, and A. M. Bradshaw, Chem. Phys. Lett. **151**, 230 (1988).

[6] I. J. Malik and M. Trenary, Surf. Sci. **214**, L237 (1989).

[7] B. N. J. Persson and R. Ryberg, Chem. Phys. Lett. **174**, 443 (1990).

[8] B. N. J. Persson and R. Ryberg, Phys. Rev. B **24**, 6954 (1981).

[9] H. Steininger, S. Lewald, and H. Ibach, Surf. Sci. **123**, 264 (1982).

[10] U. Linke and B. Poelsma, J. Phys. E **18**, 26 (1985).

[11] B. N. J. Persson, Phys. Rev. B **40**, 7115 (1989).