

Interaction of CO molecules adsorbed on stepped platinum surfaces

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Recent reflection-absorption infrared data of CO adsorbed on Pt(533) and Pt(432) surfaces are explained by a calculation of normal modes based on a dipole coupling model. The model includes electronic polarizability and field-enhancement effects, and allows for the tilted orientation of CO molecules on step sites. The low-frequency band arises from one-dimensional arrays of CO molecules on step sites; the onset of the higher-frequency band signals a transition from one-dimensional to two-dimensional arrays of CO molecules.

The adsorption of CO on two stepped platinum crystals has been studied^{1,2} with use of infrared reflection-absorption spectroscopy, low-energy electron diffraction, and temperature-programmed desorption. One crystal was cut with a (533) orientation, giving a surface with (111) terraces and (100) steps. The second was cut with a (432) orientation, giving (111) terraces and kinked steps. One of the motivations for studying these crystals was to use them as models for small catalyst particles.³ A step atom on the (533) surface has the same nearest neighbors as an edge atom in a small polyhedral crystal, whereas the kink-step atoms on the (432) crystal have the same nearest neighbors as a corner atom in a polyhedron.

The results for CO adsorption on the (533) crystal surface initially show only one vibrational band and the work reported in Refs. 1 and 2 clearly shows that it is associated with molecules adsorbed on the step atoms. At a coverage

of about 35% of the maximum coverage, a second vibration band appears, which grows with coverage as the first diminishes. At full coverage, only the second band remains, apparently containing the contributions from all of the CO molecules adsorbed on step and terrace sites. The absorption bands occur in the spectral region 2060 to 2100 cm^{-1} , characteristic of CO, linearly bonded to a single metal atom.⁴ No other bands were detected in the spectral region down to 1750 cm^{-1} . The experimental data on band positions and band intensities as functions of coverage are represented by the curves in Figs. 1 and 2.

The initial adsorption, taking place only on step atoms, provides a very nice one-dimensional system that can be modeled simply, and provides a good way to get coupling constants between adsorbed CO molecules. We calculate the in-phase vibrational frequency for an equally spaced line of N point-dipole oscillators. The wave number ν is ob-

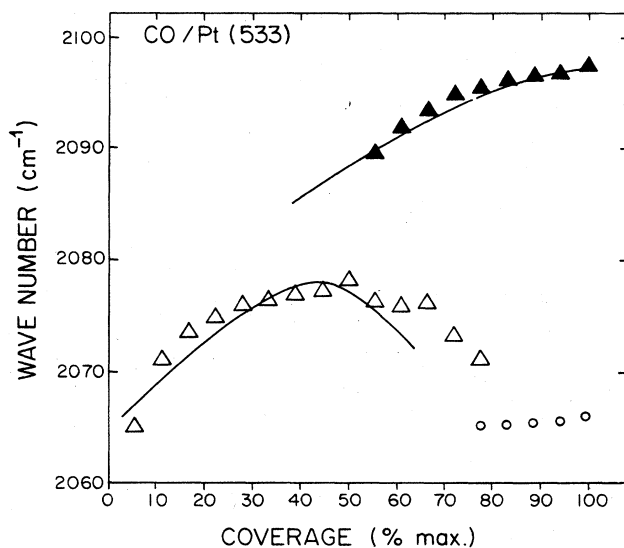


FIG. 1. The position of the two CO stretching bands of Co/Pt(533). The solid lines represent the experimentally determined band positions. The plotted points represent values calculated from the model described in this paper.

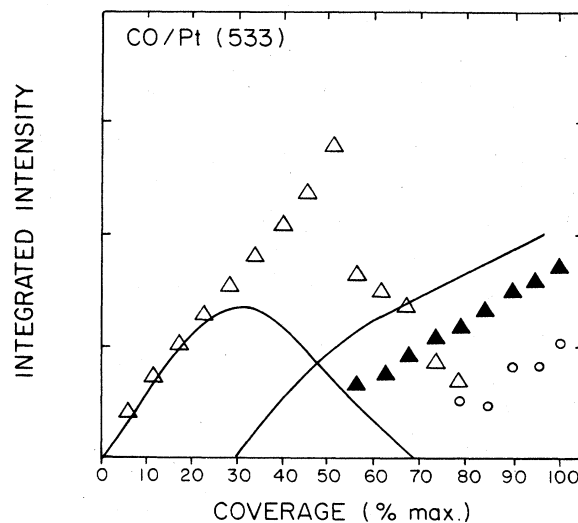


FIG. 2. The variation of integrated absorption intensity with coverage for CO/Pt(533). The solid curves represent the experimental data and the points represent values calculated from the model. Model results are normalized by matching the slope of the experimental curve at low coverage.

tained by solving the N coupled-oscillator equations,^{5,6}

$$(\nu_0^2 - \nu^2)p_i + \sum_{j=1}^N C_{ij}p_j = 0, \quad (1)$$

where p_i is the dipole moment of the i th molecule and ν_0 is the wave number of the vibration of an isolated adsorbed molecule (including self-image effects). For parallel dipoles, the nonvanishing coupling coefficients ($i \neq j$) are of the form $C_{ij} = c/d_{ij}^3$, where c is a coupling constant and d_{ij} is the distance between the i th and j th dipole.

The lower curve of Fig. 1 indicates that the wave number of the vibration of an isolated molecule (ν_0) on a step atom is 2065 cm^{-1} . We assume that the maximum of that curve (2078 cm^{-1}) is associated with an infinite string of coupled oscillators. From these wave numbers we can calculate the coupling constant c once we fix the spacing of the molecules.

On a Pt(111) plane, CO forms $(\sqrt{3} \times \sqrt{3})$ islands.⁷ We assume that on the step it forms one-dimensional islands with similar spacing. The expectation is for population of every other edge atom, resulting in a spacing of $2a$ ($a = \text{diameter of a Pt atom}$) compared with $1.73a$ for the $(\sqrt{3} \times \sqrt{3})$ islands. From such a model we calculate $c = 0.0421a^3\nu_0^2$.

We assume that, at saturation, the CO forms a $(\sqrt{3} \times \sqrt{3})$ array on the Pt terrace and step atoms as shown in Fig. 3. We first make the simple assumption that an isolated molecule on a terrace site has the same wave number as an isolated molecule on an edge site (2065 cm^{-1}). We can then calculate the frequencies and intensities of the various normal modes that result from the interaction of various configurations of molecules on edge and terrace sites. We neglect coupling between molecules on different terraces. As we consider two-dimensional islands, we find an abrupt increase in frequency for the in-phase modes. For example, an island of only four molecules (made up of molecules 1, 2, 3, and 10 in Fig. 4) has a wave number of 2088 cm^{-1} , a jump of 10 cm^{-1} from the wave number of the infinite one-dimensional string. This abrupt jump in wave number, in going from the one-dimensional regime to the two-dimensional regime, agrees with the experimental observations and explains the appearance of the second band. It results both from the increased coupling in a two-dimensional array and from the slightly smaller nearest-neighbor spacing in the two-dimensional array. The same effect is present in the more sophisticated model that we shall describe, the results from which are shown in Figs. 1 and 2. At saturation our simple model gives an in-phase vibration at 2100 cm^{-1} , which is in rather good agreement

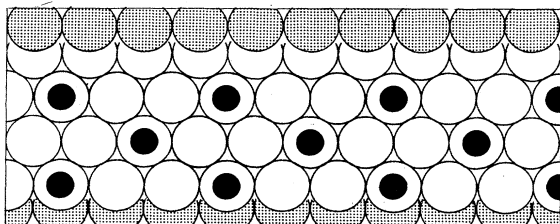


FIG. 3. The $(\sqrt{3} \times \sqrt{3})$ structure of CO adsorbed on one terrace of Pt(533).

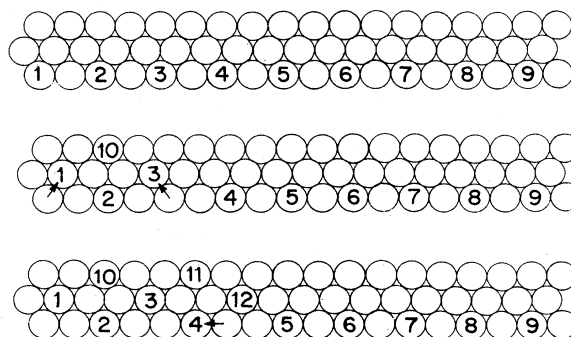


FIG. 4. Partial sequence for the adsorption of molecules in the model described in this paper.

with the measured value of 2097 cm^{-1} .

A deficiency of this simple model is that it does not predict the observed intensity variations very well. The next model incorporates four additional effects.

(1) The molecules adsorbed on the edge atoms are assumed to tilt outward at an angle from the terrace normal. We have chosen a tilt angle of molecules on step sites of 30° , similar to measurements on a stepped W surface,⁸ a stepped Ru surface,⁹ and a different stepped Pt surface.¹⁰

(2) The electronic polarizability of adsorbed molecules is included. This results in the replacement of the C matrix in Eq. (1) by the matrix $(I + \beta\nu_0^{-2}C)^{-1}C$, where I is the unit matrix and β is the ratio of electronic polarizability to vibrational polarizability. We chose $\beta = 10$, which is a typical value for CO on metals.⁶

(3) ν_0 is different for molecules on terrace sites than for molecules on edge sites. The effect of tilting the edge molecules is to reduce the coupling in the two-dimensional islands and lower the wave number of the vibration at saturation. The value of ν_0 for terrace sites is chosen to match the observed final band position and, for a tilt angle of 30° and a value of $\beta = 10$, is calculated to be 2074 cm^{-1} .

(4) Field enhancement effects at different sites are added. The electric field (from the infrared wave) should be enhanced near the step edge of the crystal surface.¹¹ Using the method of Ref. 11 we have calculated that the E field for the step atoms, the next atomic row, and the third row are in the ratio of 2.3:1.6:1.0.

In order to derive coverage-dependent values of frequency and band intensity, we have adopted a one-terrace model. We consider a section of terrace 18 atoms long, which will hold 18 adsorbed molecules when saturated. We consider this section to be repeated periodically to produce an infinitely long terrace. The molecules are added in the sequence shown in Fig. 4. The first nine molecules saturate the edge sites and (with the periodic repetition of this unit) produce an infinite one-dimensional chain. The tenth molecule, placed on the terrace, draws molecules 1 and 3 into positions appropriate for a $(\sqrt{3} \times \sqrt{3})$ island. Each additional molecule expands the two-dimensional island. Given such a sequence, we can calculate the frequencies and intensities of various modes for coverages corresponding to the addition of each of the 18 molecules. Results of the frequency calculations are shown in Fig. 1. In general, for coverages giving small, two-dimensional islands, there are two normal modes that contribute most of the intensity.

One is a higher-frequency mode, where most of the molecules of the island are vibrating in phase with significant amplitudes and the other molecules have smaller amplitudes. The other, lower-frequency mode, involves the shortened section of the one-dimensional strings of molecules adsorbed on step sites, vibrating in phase with significant amplitude, while the two-dimensional island molecules have smaller amplitudes. As the coverage increases, the one-dimensional strings get smaller and their frequencies consequently decrease. The calculated intensities of bands from this model are shown in Fig. 2.

The exact choices of the parameters used in this model are not critical. If the tilt angle of the molecules is decreased by 10° , the resulting ν_0 of terrace sites decreases by about 1 cm^{-1} . A doubling of the electronic polarizability used here will decrease the high coverage slope of the intensity-coverage curves by about 30%. Completely ignoring the field enhancement will double the high coverage slopes.

Using the parameters derived from the data on the (533) surface, we calculated the variation of band position and intensities for the (432) surface. The agreement with the data² is similar to that shown here and the calculation correctly predicts some of the details that differ between the two cases.

For the (533) surface, our model predicts, at high coverages, the existence of a band at 2065 cm^{-1} with non-negligible intensity (shown by circles in Fig. 2). This band results from a mode in which the molecules adsorbed on the step atoms are vibrating out of phase with those on the inner row of terrace atoms. If we include nearest-neighbor coupling between molecules on different terraces, this mode is reduced and shifted to lower frequency, while the frequency and intensity of the other (in-phase) mode is nearly unchanged. With the addition of interterrace coupling, at saturation our calculations show two modes with significant intensity in the region $2050\text{--}2055 \text{ cm}^{-1}$. The sum of those

intensities is only about 40% of the intensity of the in-phase mode that was measured.

The wave number of an isolated CO molecule adsorbed on a step site (2065 cm^{-1}) has been obtained from the data by extrapolating the band position to zero coverage. However, no such extrapolation can yield the wave number of an isolated molecule on a terrace site. The first terrace molecules couple to those already occupying the step sites, resulting in a significant shift in the wave number of the coupled vibration. Our model yields a value for this important parameter of 2074 cm^{-1} . It is perhaps surprising to find two molecules, bound to the surface by quite different binding energies, to have wave numbers separated by only 9 cm^{-1} . The result is consistent with the observation of only one vibration band at high coverage, indicating that molecules on the two sites have nearly the same vibrational frequencies and, hence, have strong vibrational coupling.

In summary, the existence of the two vibrational bands in the spectra of CO on stepped Pt crystals is well explained by one-dimensional and two-dimensional arrays of coupled CO molecules and a value is obtained for the wave number of an isolated CO terrace molecule. Presumably, other models that differ from this one, but which (a) include one-dimensional and two-dimensional islands and (b) assume a nearest-neighbor spacing of CO similar to that found on extended single-crystal surfaces, will show the same features as this model. The success of the coupling model in explaining these data on stepped surfaces suggests that the same approach may be useful in understanding the spectra of molecules adsorbed on small platinum particles and provides an important parameter for those calculations.

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