Adsorbate Interactions of CO Chemisorbed on Pt(111)

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Abstract

We show that the observed repulsive interaction between CO molecules on the Pt(111) surface can be explained by the coupling of the Pt–CO separation with Pt–Pt coordinates in the substrate. The observed long range of the interaction and the non-monotonic distance dependence are reproduced. The magnitude of the multiphonon decay of the Pt–CO vibration calculated in this model is also in agreement with experiment.

Keywords: Chemisorption; Platinum; Carbon monoxide; Low index single crystal surfaces

Adsorbate-adsorbate interactions are an essential aspect of potential energy surfaces in chemisorption on metal surfaces. They manifest in effects such as the formation of adsorbate islands and regular structures, they influence the shape of thermal desorption spectra, they may be very important for diffusion and reactions between adsorbates, etc.

The properties of the clean Pt(111) surface and of CO chemisorption are complex. There is large tensile stress within the first atomic layer of the clean Pt(111) surface (Ref. [1] and references therein, [2]) This is caused by an abrupt change in the electronic structure at the surface, with a consequent decrease of the optimum distance between the atoms in the first layer compared with the bulk lattice constant. The effect is not strong enough to induce reconstruction at room temperature, unlike the Pt(100) surface which reconstructs by forming a dense hexagonal layer [3,4] (although a non-reconstructed metastable Pt(100) surface can also be obtained under certain conditions). The reconstruction of the Pt(111) surface does occur at high temperatures in the presence of saturated Pt vapour [1], where a network of linear structures consisting of more densely packed atoms develops. Interestingly, the distance of the first to the second atomic layer is the same as in the bulk or even

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slightly larger, as both experimental and theoretical evidence suggests (Ref. [2] and references therein). However, at step edges the interatomic distances contract [2,5]. CO molecules adsorb initially on the on-top sites, but the energy difference for the adsorption into bridge sites is obviously rather small, so that some bridge adsorbates are found already at coverages above 0.15 [6]. Several regular adsorbate structures have been observed [7]. At a coverage of 0.29 a complex regular structure of on-top adsorbates is formed, consisting of hexagonal patches of coverage 1/3 separated by unoccupied atoms. According to Ref. [7], this is the densest structure of on-top adsorbates only, and further chemisorption occurs into bridge sites, but other authors claim that a regular \((\sqrt{3} \times \sqrt{3})R30^\circ\) structure at a coverage of 1/3 exists (Ref. [8] and references therein). The regular structure at 0.5 contains an equal number of on-top and bridge adsorbates.

The existence of regular adsorbate structures is indicative of strong interactions between the adsorbates. Furthermore, the adsorption energy decreases from around 1.9 eV at low coverages to 1.66 eV at coverage 0.33 and to 1.2 eV at half coverage [8], which means that the interaction is repulsive. There is evidence that repulsive forces exist between adsorbates several lattice constants apart, and that they depend non-monotonically upon distance [9]. Another indication of the importance of adsorbate-adsorbate interactions is the peculiar coverage dependence of the linewidth of the CO–Pt vibrations of the on-top species, which has been observed by IR spectroscopy [10].

Theoretical work on the adsorbate-adsorbate interaction has been inconclusive, apart from the general agreement that the interaction is mediated through the substrate. First-principle electronic calculations have failed to clearly identify the interactions, or have given attractive interactions, which is not in agreement with experiment [5,11]. However, such calculations have not included full relaxation of the substrate atoms upon chemisorption, either because the lateral relaxation of surface atoms is precluded by symmetry when periodic geometries are used, or because there are too many degrees of freedom to investigate relaxations and there is large intrinsic stress between substrate atoms in the case of cluster geometries.

In this paper we show that interaction energies for on-top chemisorption of CO on Pt(111), which are in agreement with experimental data, can be obtained from a model based on lateral relaxation of Pt atoms around the adsorption site, with the same distance dependence as the interaction potential.

We describe the adsorbate–substrate interaction by the Morse potential

\[
V(z - z_0) = E_0(e^{-2\alpha(z - z_0)} - 2e^{-\alpha(z - z_0)}),
\]

where \(E_0\) is the adsorption energy, \(z\) the coordinate of the CO molecule and \(z_0\) the coordinate of the Pt atom. (In our notation, the minimum of the po-
tential is at \( z - z_0 = 0 \). It would be more consistent to explicitly include the equilibrium distance \( z_0 \). For simplicity, here and in the following we omit the equilibrium distances between atoms.) The constant \( \alpha \) can be expressed as

\[
\alpha = \sqrt{\frac{\mu \Omega^2}{2E_0}}.
\]

where \( \mu \) is the reduced mass (assuming, say, a free Pt–CO complex), and \( \Omega \) the frequency of Pt–CO vibrations, which are known quantities. If we expand the potential (1) around the equilibrium, the terms linear in \((z - z_0)\) cancel, the quadratic terms give the harmonic force and higher terms give non-harmonicity. This means that by using the Morse potential we obtain an estimate (usually quite reliable) of non-harmonicity in terms of known quantities.

We extend this approach by including into the potential terms which couple the Pt–CO coordinate \((z - z_0)\) with other interatomic distances in the substrate, with the same exponential dependence as the attractive part of the Morse potential:

\[
ce^{-\alpha(z-z_0)}(x_0 - x_1).
\]

We include only the attractive part of the Morse potential because it corresponds (more or less) to the formation of the chemical bond by the valence electrons of the adsorbate and the substrate, which is expected to modify the bonding of the substrate atom to its neighbours as well. The repulsive part of the potential, on the other hand, is due mostly to the overlap of the inner (chemically inert) orbitals of the adsorbate and the substrate atom, which does not affect other bonds.

Eq. (3) expands around the equilibrium point into

\[
c(x_0 - x_1) - c\alpha(z - z_0)(x_0 - x_1) + \ldots.
\]

When added to the harmonic potential which describes the forces between other substrate atoms, the first (linear) term gives a downward shift of the minimum of the potential, i.e. a relaxation energy, and a change of the equilibrium distance in the \((x - x_0)\) coordinate, while the second (non-diagonal quadratic) term couples the motion of the \((x - x_0)\) and the \((z - z_0)\) coordinates. It has recently been argued that the non-diagonal term is large on the ground that it allows the multiphonon decay of Pt–CO vibrations [12], which would otherwise have very small probability for on-top adsorbates. We shall return to this problem further on.

The effects of the linear term may be significant or not, depending upon the nature of the \((x - x_0)\) coordinate. If \((x - x_0)\) is a distance to a Pt atom in
the second layer, its relaxation, although important in principle, is difficult to determine experimentally, while the energy gain is small compared with the total depth of the adsorption well. The situation is different if \((x - x_0)\) is the distance to another Pt atom in the first layer, i.e. a coordinate parallel to the surface. If the CO coverage is small, each adsorbed molecule may be treated independently, and more or less the same reasoning applies. However, if the adsorbate concentration is large, the presence of another CO on the second-nearest neighbour will inhibit the relaxation of the middle Pt atom in the direction parallel to the surface, as shown in Fig. 1. This means that at large CO coverages there will be no energy gain owing to relaxation, and the total adsorption energy in a dense overlayer will be smaller than for an isolated CO, i.e. there is a net repulsive interaction between adsorbates. In the following we develop a quantitative theory of the effect.

![Fig. 1. A schematic picture of CO adsorption. At a low coverage (CO molecule at position 2 only) the adjacent Pt atoms shift to a relaxed position, and participate in Pt–CO vibrations (grey arrows). At high coverages (positions 1 and 3 also occupied), the Pt atoms in between the adsorption sites can neither relax laterally, nor can they participate in vibrations if all CO adsorbates vibrate in phase.](image)

We conclude these introductory remarks by noting that the quantitative aspect of the described approach has all virtues and problems inherent to the use of the Morse potential for describing chemisorption. Ultimately, only first-principle calculations can show how large the deviations of a more realistic potential from the Morse function are.

In our model we include only the first atomic layer of the Pt(111) surface, with one or two CO molecules adsorbed on it. We consider the motion perpendicular to the surface (\(z\)-direction) only for the Pt–CO complex (coordinates \(z_0\) and \(z\); the C–O bond is assumed rigid), and only the motion parallel to the surface of the other Pt atoms (coordinates \(\vec{r}_i = (x_i, y_i)\)). The complete Hamiltonian in the harmonic approximation for one adsorbate is

\[
H = T + V, \quad (5)
\]
where $T$ is the kinetic energy:

$$ T = \frac{1}{2} m \dot{z}^2 + \frac{1}{2} M \dot{z}_0^2 + \frac{1}{2} \sum_i M_i \dot{r}_i^2 $$

(6)

and $V$ is the potential energy:

$$ V = \frac{1}{2} K z_0^2 + \frac{1}{2} k (z - z_0)^2 + \frac{1}{2} \sum_i \sum_{j=1}^6 \frac{1}{2} K_1 \hat{r}_{ij} \cdot (\hat{r}_i - \hat{r}_j)^2 + \frac{1}{2} \sum_i K_2 \hat{r}_i^2 
+ \sum_{j=1}^6 k_1 (z - z_0) \hat{r}_{0j} \cdot (\hat{r}_0 - \hat{r}_j) - \sum_{j=1}^6 \frac{k_1}{\alpha} \hat{r}_{0j} \cdot (\hat{r}_0 - \hat{r}_j). $$

(7)

Here the index $i$ runs over surface atoms, $i = 0$ being the adsorption site, the index $j$ runs over the six Pt atoms around the atom $i$, and $\hat{r}_{ij}$ is a unit vector along the direction from $i$ to $j$. The Hamiltonian for two CO adsorbates is obtained by introducing another set of $z$-dependent terms at another site $i$.

The kinetic energy terms are self-explanatory. The potential energy terms with the force constants $K_1$ and $k$ describe, respectively, central harmonic forces between neighbouring atoms in the $x$–$y$ plane, and between a Pt atom and the CO molecule in the $z$ direction. The term with a force constant $K$ is the coupling of the Pt–CO complex to a rigid ‘hard wall’ which describes the Pt bulk, and the term with $K_2$ couples the $x$–$y$ motion of Pt atoms to their equilibrium positions, i.e. to the atoms in the second layer, which are again assumed to be rigid. The last two terms with a force constant $k_1$ are the off-diagonal coupling of the Pt–CO bond to the surrounding Pt atoms, as explained in deriving Eqs. (3) and (4).

It is necessary to include the $K_2$ term, because the model with forces only between the atoms in the first layer (i.e. the $K_1$ term) gives a response which is too soft, since it only has an acoustic branch of vibrations in the $x$–$y$ plane, whereas most of the density of states for motion in the $x$–$y$ plane on a real surface is at finite frequencies even at small wavevectors. The masses $m$ and $M$ in Eq. (6) are those of CO and Pt, respectively. The values of the force constants $K_1 = 0.65 \times 10^5$ dyn/cm, $K_2 = 0.2 \times 10^5$ dyn/cm, and $k = 3.05 \times 10^5$ dyn/cm are chosen so as to reproduce the frequency of Pt–CO vibrations ($\sim 58$ meV [10]) and typical phonon frequencies (from $\sim 6$ meV to $\sim 24$ meV [13,14]), and $\alpha$ is given by Eq. (2). This is a sufficient minimal model for our problem, because we need the response of surface atoms to an external force, i.e. an average quantity, rather than the complete vibrational spectrum, although it would be a poor description of surface phonons for most other purposes.

We are now in a position to calculate the relaxation energies by finding the minimum of the potential energy $V$, Eq. (7). We performed the calculations
for a single adsorbed CO molecule, and for two CO molecules adsorbed on, in turn, second, third, fourth and fifth nearest-neighbour sites. We did not consider first nearest-neighbour adsorbates, since these are not observed in experiment. We used finite clusters of Pt atoms, as shown in Fig. 2 for the third nearest-neighbour case, keeping the outermost Pt atoms (grey) fixed. Full convergence of the relaxation energy was obtained using about ten layers of Pt atoms around the adsorption site. As already mentioned, the relaxation is incomplete when the adsorbates are nearby, since the two of them act on one or more Pt atoms with forces in opposite directions. We denote the relaxation energy for a single adsorbate by $E_0$, for two atoms on second nearest-neighbour sites by $E_{2\text{NN}}$, etc. The interaction energy is defined as $W_{2\text{NN}} = 2E_0 - E_{2\text{NN}}$, i.e. the difference in energy when the two adsorbates are on second nearest-neighbour sites and when they are far apart.

![Fig. 2. The geometry of Pt clusters used in the calculations, for CO adsorption on third nearest-neighbour sites (black circles). The outermost Pt atoms (grey) are kept fixed, whereas others are allowed to relax. Other adsorption sites for which calculations have been performed are indicated by numbers. The shapes of the clusters are adjusted accordingly.](image)

In Table 1 we give the calculated values of the interaction energies. We have chosen the value of the only remaining parameter in the model, the off-diagonal force constant which couples the Pt–CO and Pt–Pt coordinate, $k_1 = 0.35 \times 10^5$ dyn/cm, so that good agreement with experimental values is obtained. To our knowledge, the only other value proposed for this quantity is $k_1 = 0.141 \times 10^5$ dyn/cm, as reported in Ref. [15]. It was used in calculating the eigenfrequencies of various modes of CO/Pt(111) vibrations, in particular hindered translations, observed experimentally in helium scattering experiments. However, this force constant in Ref. [15] was of minor importance, as shown by the fact that it was taken over unchanged from a study of vibrations of CO on Ni(100) [16], where, in turn, it was assumed to be equal to the value of the
Table 1
Interaction energies, in eV. $W_{2\text{NN}} = 2E_0 - E_{2\text{NN}}$, where $E_0$ is the relaxation energy of a single CO molecule, $E_{2\text{NN}}$ is the relaxation energy for two CO molecules adsorbed at second nearest-neighbour sites, etc.

|       | $W_{2\text{NN}}$ | $W_{3\text{NN}}$ | $W_{4\text{NN}}$ | $W_{5\text{NN}}$ | $E_0/6$ |
|-------|------------------|------------------|------------------|------------------|--------|
| Theory| 0.015            | 0.031            | 0.012            | 0.014            | 0.051  |
| Experiment | 0.010$^1$ | 0.034$^1$ | 0.020$^1$ | | 0.039$^2$ |

$^1$Ref. [9], low CO coverage.
$^2$Ref. [8], CO coverage of 0.33.

CO–Pt–CO force constant of nickel carbonyl. Thus it obviously cannot be considered a reliable estimate for the CO/Pt(111) system.

We have compared our results for the interaction energies with two published sets of data. The values in Ref. [9] were obtained by analysing the experimental adsorption isotherms using a transfer-matrix approach. They are for low coverages of adsorbed CO, up to 10%. The value in Ref. [8] is obtained from the change of the adsorption energy between a low coverage and a coverage of 0.33, which corresponds to a regular ($\sqrt{3} \times \sqrt{3}$)R30$^\circ$ structure of on-top adsorbed CO molecules. Since in this structure no lateral relaxation of Pt atoms is possible, we compare this interaction energy with one-sixth of our relaxation energy for a single CO.

Overall, the quantitative agreement of our results with experiment is good. We have obtained the same non-monotonic dependence of the interaction energies as in Ref. [9]. The repulsive interaction is particularly large when the two adsorption sites lie along a row of Pt atoms, i.e. in the case of third and fifth nearest neighbours. In Ref. [9] the fifth nearest-neighbour site is not taken into account, but an accordingly larger interaction between the fourth nearest-neighbour adsorbates is obtained. We have calculated that the relaxation of the position of the six surrounding Pt atoms for an isolated CO adsorbate is $\Delta x = 0.07 \, \text{Å}$, or about 3% of the nearest-neighbour Pt–Pt distance. There are no experimental data to compare with, but this value is similar to the calculated relaxation of Pt atoms on step edges upon CO chemisorption [5]. Also, the change in Pt–CO distance obtained, 0.05 Å, is close to the value calculated in Ref. [17].

Next, we briefly address the multiphonon decay of Pt–CO vibrations. The present approach has already been used in Ref. [12], but we are now able to obtain a more quantitative estimate. As the energy of Pt–CO vibrations at 58 meV is high above the largest energy of Pt phonons, at about 24 meV, the decay can occur only via anharmonicity-mediated three-phonon (or higher order) processes. Assuming that the dominant anharmonicity is that of the Pt–CO bond, the anharmonic terms can be found expanding the Morse po-
tential (1) beyond the harmonic approximation. Since these terms are small, the multiphonon transitions can be evaluated perturbatively after the harmonic Hamiltonian (5) is diagonalized.

We denote the initial coordinates by a vector $x = (z, z_0, x_i, y_i)$, the transformed ones by $v = (u, v_i)$, the mass matrix corresponding to the kinetic energy (6) by $T$ and the orthogonal transformation matrix by $A$:

$$v = A^\dagger T^{1/2} x.$$  

(8)

The matrix $A$ transforms the Hamiltonian (5) into the diagonal form

$$H = \frac{1}{2} u^2 + \frac{1}{2} \Omega^2 u^2 + \sum_i \left( \frac{1}{2} v_i^2 + \frac{1}{2} \omega_i^2 v_i^2 \right),$$

(9)

where $\Omega$ is the large frequency corresponding to the CO–Pt vibration and $\omega_i$ are smaller ‘phonon’ frequencies. We express the Pt–CO coordinate in terms of the diagonalized modes:

$$z - z_0 = gu - \sum_i h_i v_i.$$  

(10)

The coefficient $g$ is large, whereas $h_i$ are small, expressing the fact that the phonon modes which couple to Pt–CO vibrations have only a small admixture of the Pt–CO coordinate.

We now insert (10) into the anharmonic terms $(z - z_0)^3, (z - z_0)^4$, etc., obtained from the expansion of the Morse potential, and obtain products of various powers of $gu$ and $h_i v_i$. The dominant contribution to the vibrational decay comes from three-phonon processes, i.e. from transition probabilities from an initial state $|i\rangle$ consisting of a singly excited $u$ (Pt–CO) vibration to a final state $|f\rangle$ with $u$ in the ground state and three excited phonon states $v_i$ such that the total energy is conserved. The transition probability is

$$P_{if} = \frac{2\pi}{\hbar} |\langle i | H' | f \rangle|^2 \delta (E_i - E_f),$$

(11)

where $H'$ is the anharmonic part of the Morse potential (1) (essentially $uv_1 v_2 v_3$), and the total decay width is

$$\Gamma = \hbar \sum_f P_{if}.$$  

(12)

According to (10), $P_{if}$ is proportional to $(gh_1 h_2 h_3)^2$. In the case of no off-diagonal coupling, $k_1 = 0$, in our model there is only one $h$ and, to leading order, the coefficients are

$$g = \frac{1}{\sqrt{m}}.$$
\[ h = \frac{1}{\sqrt{M}} \left( \frac{\omega}{\Omega} \right)^2. \]  \hspace{2cm} (13)

(Of course, the energy conservation cannot in general be satisfied in the model with only one phonon coordinate \( v \), but the same conclusion holds if the model is generalized introducing a projected phonon density of states \( \rho(\omega) \), as in Ref. [12].) The frequency ratio in (13) is the ‘reduction factor’, which makes the decay probability too small by about five orders of magnitude [10]. This result led to a conclusion that other mechanisms, such as electron-hole pair excitation, must be dominant in the decay of Pt–CO vibrations.

Our suggested value of the off-diagonal force constant \( k_1 \) is large enough to completely change this situation. When this term is included, we obtain many phonon modes \( v_i \) with couplings \( h_i \). The frequencies are still discrete and the model is not realistic enough to calculate the total decay numerically. We therefore just calculate the enhancement of the ratio

\[ \sum_i \left( \frac{h_i}{g} \right)^2 \]  \hspace{2cm} (14)

with respect to the case with \( k_1 = 0 \), which turns out to be 44.4. The total enhancement of the decay probability via three-phonon processes is the third power of this value, or \( 0.88 \times 10^5 \), which is again about the right magnitude as the experimental values, according to the estimates of Ref. [10].

Thus we find that the three-phonon decay of the Pt–CO vibrations for a single adsorbate agrees with the observed linewidth, and no other decay processes (or other mechanisms which increase the width) need to be involved. Furthermore, the phonon mechanism can explain the observed coverage dependence of the linewidth, as discussed in Ref. [12]. The efficiency of the decay depends upon the ability of the surrounding Pt atoms to move laterally following the Pt–CO vibration, in much the same way as their ability to have a static relaxation shift determines the contribution to the adsorption energy. In infrared spectroscopy experiments, CO atoms move in phase over very large distances, and in dense adsorbate structures there are few or no atoms which can move laterally and contribute to the decay of the Pt–CO vibrations. This is in agreement with the observed minimum of the adsorption width at a coverage of 0.3 [10], whereas the width is large at a coverage of 0.19, corresponding to a less dense regular structure. If the width were due to inhomogeneous effects, one would expect the converse.

To conclude, we have shown that the interaction between CO molecules adsorbed in on-top positions on the Pt(111) surface is associated with the lateral relaxation of the surrounding Pt atoms, and that a good quantitative description is obtained by choosing an appropriate value of the relaxation. The model is further corroborated by the fact that it gives a value for the multiphonon de-
cay of Pt–CO vibrations which is in agreement with the vibrational linewidth observed experimentally. This approach predicts that the interaction between equivalent species will usually be repulsive, since some surface atoms will not be able to relax completely. This is indeed the case for on-top CO on Pt(111) considered here [9], and also for CO in three-fold hollow sites on Ni(111) [18]. Non-equivalent species, however, may interact attractively if the relaxation forces act in the same direction on some surrounding surface atoms, increasing the total relaxation energy. This appears to be the case between coadsorbed CO in on-top and NO in bridge positions on Pt(111), and presumably also between on-top and bridge CO which occur on Pt(111) at higher coverages. We intend to pursue a quantitative investigation of these systems.

Acknowledgements

This work was supported by the Ministry of Science and Technology of the Republic of Croatia under the contract Nr. 00980102.

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