

# Adsorbate-induced substrate relaxation and the adsorbate–adsorbate interaction

R. Brako \*, D. Šokčević

*Rudjer Bošković Institute, PO Box 180, 10002 Zagreb, Croatia*

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## Abstract

We formulate the theory of the relaxation of the substrate lattice induced by a chemisorbed molecule, using the quadratic expansion of the potential energy of a free surface. We assume that the adsorbate introduces local perturbations around the adsorption site and calculate the relaxation of the surrounding substrate atoms, the induced surface stress and the relaxation energy. When two adsorbates occupy nearby sites, the relaxation is incomplete, leading to an effective adsorbate–adsorbate interaction. We show that the interaction energy has a non-monotonic dependence upon the adsorbate–adsorbate separation, characteristic of each low-index surface. Using simple models of the substrate lattice potential, it is possible to deduce the strength of the perturbation. Good agreement is obtained with experimental data on the induced stress and the adsorbate–adsorbate interaction of CO chemisorbed on several closely packed metal surfaces. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Several direct and indirect (through-the-substrate) mechanisms can lead to an effective interaction between adsorbates on metal surfaces. Direct mechanisms are those that also exist between molecules in the gas phase, although they may be quantitatively modified on surfaces. They are usually short-ranged or weak, e.g. the repulsion due to the overlap of electronic orbitals is strong but limited to small distances, and the Van der Waals attraction and electrostatic multipole interactions are weak. Through-the-substrate mechanisms depend upon the fact that each adsorbate

modifies the properties of the substrate around the adsorption site, perturbing the conduction and valence electrons and the lattice. Both effects have been observed experimentally, i.e. localized relaxations of the substrate lattice around the adsorption site have been determined, and oscillations of conduction electron density have been observed using scanning tunnelling microscopy. If the adsorbates are close enough, the perturbation caused by one adsorbate influences the other, and the total energy is not exactly the sum of the relaxation energy of isolated adsorbates, i.e. an effective interaction energy appears.

The electronic and lattice perturbations are related and cannot be strictly separated. We shall nevertheless refer to ‘electronic’ and ‘phonon-mediated’ interaction mechanisms in the following sense. The adsorbate–substrate chemical bond

\* Corresponding author. Fax: +385-1-4680-223.

E-mail address: radovan.brako@irb.hr (R. Brako)

strongly perturbs the substrate atom at the chemisorption site (or two atoms in the case of bridge chemisorption site, etc.). The induced relaxation causes a change of equilibrium distances from neighbouring atoms, which leads to a long-range elastic distortion of the lattice around the chemisorption site. Similarly, the strong primary electronic perturbation causes a tail (possibly of oscillatory nature) of perturbed electronic orbitals. We make the distinction based on which one of the two long-range perturbations influences the relaxation energy of the second adsorbate more strongly. (We are not really interested in the case when the two adsorbates are so close that the primary regions of strong perturbations touch, when the effect is likely to be highly non-linear, leading either to a strong repulsion, or to a recombination of some kind.) In this paper, we argue that there is evidence that the lattice distortion, i.e. the phonon-mediated interaction, is dominant in many well-known chemisorption systems.

In Section 2, we further discuss the perturbations of the substrate induced by an adsorbate and the resulting adsorbate–adsorbate interaction. In Section 3, we formulate a theoretical approach to the phonon-mediated adsorbate interaction, starting from the potential energy of a clean substrate in the harmonic approximation, and introducing the perturbation induced by the adsorbate. We calculate the quantities of interest, i.e. the induced surface stress, the relaxation energy and the adsorbate–adsorbate interaction energy. In Section 4, we first discuss the general properties of closely packed transition metal surfaces. We then formulate simple models that describe the first layer of surface atoms, interacting via central harmonic forces. We use the models to calculate experimentally observable quantities, in the first place, the adsorbate-induced surface stress and the interaction energies, and compare them with experimental data on CO adsorbed on several transition metal surfaces. In Sections 5 and 6, we discuss the results and formulate the conclusions.

## 2. Interaction of adsorbed molecules

The prospect of explaining the chemisorption of molecules on metal surfaces by first-principle

electronic calculations is attractive, but the applicability of the method is limited by the numerical complexity of the problem. The calculations have made it possible to understand the character of the chemical bond for a variety of systems. For high adsorbate coverages, half a monolayer or more, which can be described by a small surface unit cell, it is possible to obtain detailed information about the geometry and the energetics of the chemisorption. Thus, for O chemisorption on Rh(110), the equilibrium configurations, work function, chemisorption energies, and possible reconstructions have been determined at coverages of 0.5, 1, and 2 monolayers [1]. Similarly, a calculation of O chemisorption on Rh(001) at half a monolayer coverage suggested a reconstruction involving a rhomboid distortion of the substrate atoms around the fourfold hollow adsorption sites [2]. At lower coverages, and especially for an (almost) isolated adsorbate, the quantitative accuracy is difficult to achieve, as cluster calculations suffer from uncertainties caused by finite-size effects, while calculations with periodic boundary conditions quickly become untractable because of the large cell size. Thus, calculations of the relaxation of substrate atoms (especially in the lateral directions) for an isolated adsorbate or of the energy of interaction between two adsorbates on an otherwise clean surface are scarce. Recently, Brivio and Trioni [3] have reviewed the progress in *ab-initio* methods for calculating the electronic properties of a single isolated molecule adsorbed on a metal surface. They also discuss some results on electronic lateral interactions between adsorbates. More progress can be made with simpler models, e.g. the free-electron model or the tight-binding model of substrate electrons, and the lattice dynamic theory for the atomic degrees of freedom. The parameters, such as the geometry of the adsorption site, the interatomic distances, the magnitude of the substrate relaxation, the strength of the chemical bond, etc., can be extrapolated with various degrees of confidence from experimental data or from available first-principle calculations.

The possibility that the strain induced by adsorbates leads to an effective adsorbate–adsorbate interaction has been discussed in the literature on

several occasions. In one approach, the substrate is treated as an elastic continuum, and the bulk elasticity tensor is used. It is interesting to note that two defects in an infinite isotropic elastic medium do not interact, if the stress induced by each defect is centrally symmetric. The same holds in two dimensions, i.e. for an elastic sheet. If the symmetry is lower, e.g. for defects on the surface of a semi-infinite medium, or for a ‘multipolar’ induced stress, the interaction energy is non-zero. Lau and Kohn [4,5] found that the interaction was repulsive between two identical adsorbates on a surface, that it varied as  $\rho^{-3}$  with separation  $\rho$ , and was inversely proportional to the shear modulus of the substrate. A similar approach has recently been used by Peyla et al. [6].

The elastic continuum approach breaks down at small adsorbate–adsorbate distances, i.e. a few lattice spacings, which is the most interesting region. Also, force constants between atoms within the top surface layer are often strongly modified compared with those in the bulk, which cannot be easily taken into account in the continuum model. In such cases, the discrete lattice dynamics model is more appropriate. Tiersten et al. [7,8] used a lattice dynamics approach to calculate the interaction between As dimers and O atoms on a Si(100) surface. They found that the interaction energies had a non-monotonic dependence on adatom separation and a strong dependence on direction. Recently, in a series of papers, Kevan et al. [9–13] have determined adsorbate–adsorbate interaction energies for CO at several metal surfaces, analysing thermal desorption spectra using a transfer-matrix method. They have also qualitatively discussed the adsorbate-induced strain as a possible mechanism of the adsorbate–adsorbate interaction.

The electronic mechanism has also been extensively studied. In a recent review, Einstein [14] has discussed various theories of the electronic adsorbate–adsorbate interaction and has also given a short survey of the work on lattice-mediated mechanism. Lau and Kohn [15] have found that the asymptotic behaviour of the interaction mediated by conduction electrons with a spherical Fermi surface is proportional to  $\cos(2k_F R)/R^5$ , but can have a longer range,  $\sim \cos(2k_F R)/R^2$ , if a partially

filled surface band exists. The oscillatory dependence upon the separation,  $R$ , the important role of the sharp discontinuity at the Fermi surface (which enters through  $k_F$  in the spherically symmetric case), and the decay of the envelope with  $R$  as an inverse power are characteristic features that are common to almost every calculation of the electron-mediated adsorbate interaction. The exponent of the power depends upon details of the system, and the decay can be as slow as  $1/R$  in the interaction mediated by quasi-one-dimensional electronic states on reconstructed (110) surfaces of fcc metals, e.g. Ni and Cu [16,17]. The strength of the interaction also depends very much on details of the model, but it has been estimated in some cases to be large enough (0.1 eV and more) to account for the interaction energies observed experimentally between second- or third-nearest-neighbour adsorbates. In this paper, we focus on the phonon-mediated interaction, but we keep in mind that the electronic interaction can be important in some cases and that more work will be necessary in order to clarify the question related to particular systems.

In this paper, we use the harmonic approximation of the potential energy of the lattice and assume that the adsorbate induces additional linear and quadratic terms. Since the dynamical matrices of many bulk materials are well known and the perturbation is rather localized, one may expect that the magnitude of the additional terms can be deduced easily. It turns out that the problem is not so simple, since the force constants and off-diagonal couplings in the first surface layer are known with much less certainty than the bulk values. In order to circumvent this problem, in this article, we try to identify those adsorbate-induced quantities that depend upon the geometry of the surface and of the adsorption site and not much on the quantitative values of the parameters. We show that a particularly characteristic property is the non-monotonic distance dependence of the adsorbate–adsorbate interaction. Specifically, there is a large repulsion between on-top adsorbates, which lie along the same row of substrate atoms. The interaction is weaker in other cases (hollow sites, different rows) and occasionally is weakly attractive.

In Refs. [18,19], we have used similar models to show that the coupling of the adsorbate–substrate distance with the in-plane displacement of surrounding surface atoms can be important in the multiphonon decay of adsorbate vibrations. In Ref. [19], we have also calculated the resulting effective adsorbate–adsorbate interaction. In the present paper, we use the potential energy of the same form as in the Hamiltonian in Ref. [19], but we also calculate the adsorbate-induced surface stress. This introduces more stringent conditions upon the values of the parameters in the potential energy and constitutes a further test of the validity of the model. A short account of this work has been given in Ref. [20].

### 3. Theory of the phonon-mediated adsorbate–adsorbate interaction

The harmonic expansion of the potential energy of the atomic lattice of a solid can be written as

$$V = \sum_{i,j,\mu,\nu} x_\mu(i) D_{\mu\nu}(i,j) x_\nu(j), \quad (1)$$

where  $x_\mu(i)$  is the  $\mu$ th component of the displacement of the  $i$ th atom from the equilibrium position, and  $D_{\mu\nu}(i,j)$  is the dynamical matrix. We have set the energy zero at the minimum of  $V$ .

Now, assume that one atom in the lattice is replaced by a different species, i.e. an ‘impurity’ is introduced. (We are, in fact, interested in the case when an atom or a molecule adsorbs onto an initially clean surface. Since we calculate only the ground-state properties, we do not worry about the adsorbate–substrate and internal adsorbate degrees of freedom, and use the simpler approach in which the adsorption site is treated as an ‘impurity’.) The potential energy of the modified system in the harmonic approximation is analogous to (1):

$$V' = \sum_{i,j,\mu,\nu} x'_\mu(i) D'_{\mu\nu}(i,j) x'_\nu(j) + E'. \quad (2)$$

The primes denote that the equilibrium positions change and that the dynamical matrix  $D'_{\mu\nu}(i,j)$  is modified. A constant term,  $E'$ , appears and shifts the energy minimum. We can express the new

equilibrium positions using old ones:

$$x'_\mu(i) = x_\mu(i) + \Delta x_\mu(i). \quad (3)$$

Inserting this into Eq. (2), we obtain the new potential energy in old coordinates (i.e. measured from unperturbed equilibrium positions)

$$V' = \sum_{i,j,\mu,\nu} x_\mu(i) D'_{\mu\nu}(i,j) x_\nu(j) + \sum_{i,\mu} F_\mu(i) x_\mu(i) + E''. \quad (4)$$

The linear terms can be interpreted as forces appearing upon chemisorption.

These considerations are very general, and depend only upon the existence of stable minima of the potential energy. In order to make use of them in practical applications, we must assume that the change to the potential energy upon chemisorption is limited to the immediate neighbourhood of the adsorption site and can be described by a small number of parameters.

In this paper, we specifically assume the following simplifying properties:

1. Only a few force terms,  $F_\mu(i)$  are non-zero for a small number of substrate atoms around the adsorption site, and similarly, only a few elements of the dynamical matrix  $D_{\mu\nu}(i,j)$  change, if any.
2. The effect is linear. This means that the chemisorption of another molecule (and, consequently, of a third, a fourth, etc.) can be described by the same set of parameters, of course centred around the new adsorption site. Condition (2) is rather restrictive. For example, it excludes systems that reconstruct at large adsorbate coverage, as well as those where other interactions are important, such as the direct adsorbate–adsorbate repulsion, the electrostatic dipole–dipole interaction, or the ‘chemical’ competition for the same electronic orbitals in the substrate. However, (2) should be valid for a wide class of non-ionic adsorbates at intermediate distances, i.e. second-nearest neighbour and beyond.

The dynamical matrix,  $D_{\mu\nu}(i,j)$  for the bulk is well known from the phonon spectrum. However, if the atoms  $i,j$  are near the surface, the values are rather uncertain, as are the changes occurring upon chemisorption, i.e. the modified matrix  $D'_{\mu\nu}(i,j)$ . Turning to other parameters in Eqs. (1)–

(4), the force terms  $F_\mu(i)x_\mu(i)$  are central to our theory. We show that it is possible to estimate their magnitude from the observed adsorbate-induced stress and adsorbate–adsorbate interactions, even when there are no data from first-principle electronic calculations. The constant energy terms  $V'$  and  $V''$  are not known with sufficient accuracy, but they are the same for all adsorbate configurations if the linearity assumption (2) is satisfied and do not affect the interaction energies.

The definition of the chemisorption-induced surface stress tensor  $\tau$  is [21]

$$\delta W = A\tau_{ij}\delta\epsilon_{ij}, \quad (5)$$

where  $A$  is the surface area,  $\delta\epsilon_{ij}$  the strain and  $\delta W$  the difference of the work involved in straining a clean surface and a surface with adsorbates. One can easily calculate the induced stress by applying this definition to the potential energy without adsorbates (1) and with adsorbates (4). With our linearity assumption, the induced stress is proportional to the concentration of adsorbates.

By finding the minimum of the potential energy (4), one can determine the relaxation of atoms around the adsorption site and the associated energy gain. Usually, the relaxation energy cannot be directly compared with experiment, since it is a minor correction to the large chemisorption energy. However, it gives a fair estimate of the error, which is made in first-principle electronic calculations if the full relaxation of the substrate is not taken into account. As the relaxation energy can be significantly different for various sites (e.g. on-top vs. bridge vs. hollow site), the prediction of the most stable site in such calculations may be wrong.

The interaction energy between two adsorbates can be calculated by comparing the total relaxation energy for two adsorbates far apart and, say, adsorbed on second-neighbour sites, etc., assuming that the superposition condition (2) holds. In most cases, the forces induced by the two adsorbates act in opposite directions, and the relaxation is less complete than with adsorbates far apart, i.e. the interaction is repulsive. In a few cases, the induced forces are partly collinear, leading to an energy gain and an effective attractive interaction.

Useful insight into some properties of our model can be gained by considering a single harmonic

oscillator perturbed by a linear force term:

$$V = \frac{K}{2}x^2 - Fx. \quad (6)$$

Due to the force,  $F$ , the minimum of the potential energy is lowered (irrespective of the sign of  $F$ ) by

$$\Delta E = -\frac{F^2}{2K} = -\frac{F}{2}\Delta x, \quad (7)$$

where  $\Delta x$  is the new equilibrium position of the coordinate  $x$ . In the coupled harmonic model formulated in Eqs. (1)–(4), the interaction energy between two adsorbates at close distances is the departure of the total energy gain caused by the frustration of the relaxation from the value  $2\Delta E$  when the adsorbates are far apart. Similarly to Eq. (7), the relaxation and interaction energies also depend quadratically upon the force terms  $F_\mu(i)$  and are roughly inversely proportional to the force constants between substrate atoms in the first layer. As shown further on, the adsorbate-induced surface stress is proportional to the forces  $F_\mu(i)$ . These basic relationships between the measurable quantities and the parameters of our model allow rough estimates of the relaxation.

#### 4. Adsorbates on low-index metal surfaces

##### 4.1. Properties of closely packed surfaces of noble metals

There is a large tensile stress within the first atomic layer of many closely packed noble metal surfaces, which is caused by the abrupt change in the electronic structure at the surface. As a consequence of a lower coordination, the optimum distance between the atoms in the first layer is smaller than the bulk lattice constant. In some cases, the mismatch is large enough for the surface to reconstruct, as in the well-known case of Pt(100) surface, which forms a dense hexagonal layer, although a non-reconstructed metastable Pt(100) surface can be obtained under certain conditions. The reconstruction is also lifted upon chemisorption of several species, which means that, as a rule, chemisorption relieves the stress. On

other surfaces, the stress is not large enough to cause reconstruction. The Pt(111) surface reconstructs only at high temperatures in the presence of saturated Pt vapour [22], where a network of linear structures consisting of more densely packed atoms develops. Interestingly, on this surface, the distance of the first to the second atomic layer is the same as in the bulk or even slightly larger, as both experimental and theoretical evidence suggests (Ref. [23] and references therein).

We intentionally keep the models of the lattice dynamics of surface atomic layers fairly simple. We consider only the in-plane adsorbate-induced forces and relaxations. Of course, the relaxation perpendicular to the surface can be equally large, but it does not contribute much to the quantities that we calculate. In numerical calculations, we assume that the force constants (i.e. the dynamical matrix,  $D$ ) are not modified upon chemisorption. Our intention is to look for qualitative features that are model-independent as much as possible. The force constants between atoms at the surface are poorly known, and the qualitative conclusions are not affected by their change upon chemisorption. We comment further on this subject in Section 5.

#### 4.2. On-top adsorbates on (111) surfaces of fcc metals: CO on Pt, Rh, Cu

The first layer of a fcc (111) surface is a closely packed hexagonal structure. We write the potential energy as

$$V = \frac{1}{2} \sum_i \sum_{j=1}^6 \frac{1}{2} K_1 [\hat{r}_{ij}(\mathbf{r}_i - \mathbf{r}_j)]^2 + \frac{1}{2} \sum_i K r_i^2, \quad (8)$$

where  $\mathbf{r}_i = (x_i, y_i)$  is the in-plane displacement from the equilibrium position of the  $i$ th atom. The term  $K_1$  describes a central atom–atom interaction, and the term  $K$  binds atoms to their equilibrium positions, simulating the interaction to lower atomic layers. Without it, the model would be too ‘soft’ to long-wavelength perturbations. The trade-off is that the lowest phonon frequency becomes finite, i.e. there are no true ‘acoustic’ modes. As a consequence, at large distances, the strain falls off exponentially rather than as a power. However,

this asymptotic behaviour has little influence on the relaxation energy, the interaction energy between adsorbates at intermediate distances, and other quantities calculated in this work.

Now, assume that an atom or a molecule chemisorbs on top of the atom  $i=0$ , and that the induced change of the potential energy involves only first neighbours

$$\Delta V = \sum_{j=1}^6 \frac{1}{2} \Delta K_1 [\hat{r}_{0j}(\mathbf{r}_0 - \mathbf{r}_j)]^2 - \sum_{j=1}^6 F_1 \hat{r}_{0j}(\mathbf{r}_0 - \mathbf{r}_j) + V'_0, \quad (9)$$

where the first term describes the change of the force constant between the atom 0 and the six surrounding atoms, and the second is a linear force term. We choose the energy zero by putting  $V'_0=0$ , since we are only interested in energy differences for various adsorbate configurations. If the elastic properties around the chemisorption site do not change,  $\Delta K_1=0$ , the chemisorption-induced surface stress depends only upon the force  $F_1$  and the nearest-neighbour distance,  $a$ :

$$\tau_x = -\frac{F_1}{a} 2\sqrt{3}\theta, \quad (10)$$

where  $\theta$  is the adsorbate coverage.

On Pt(111), CO molecules adsorb initially on the on-top sites, but the energy difference for the adsorption into bridge sites is obviously small, and some bridge adsorbates are found already at coverages above 0.15 [24]. Several regular adsorbate structures have been observed [25]. 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. [25], 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 (Fig. 1) (Ref. [26] and references therein). The regular structure at 0.5 contains an equal number of on-top and bridge adsorbates. The existence of regular structures is indicative of strong interactions between the adsorbates. Furthermore, the adsorption energy

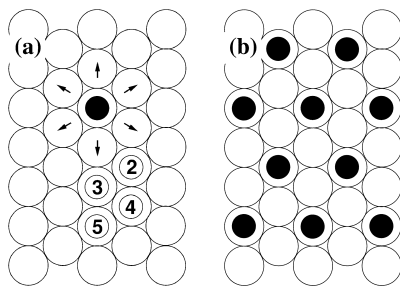


Fig. 1. (a) Chemisorption of CO, black circle, into an on-top site on Pt(111). The chemisorbate causes a relaxation of the adjacent Pt atoms, denoted by arrows, which propagates to further first-layer atoms via elastic forces. The neighbouring adsorption sites are indicated by numbers. (b) Regular  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure at a coverage  $\theta=0.33$ . Owing to symmetry, no relaxation of substrate atoms along the surface plane is possible.

decreases from around 1.9 eV at low coverages to 1.66 eV at a coverage of 0.33 and to 1.2 eV at half coverage [26], which means that the interaction is repulsive.

The value of the force  $F_1$  can be uniquely determined from the measured values of the adsorbate-induced surface stress [21], using Eq. (10). We have calculated the relaxation energy and the interaction energies by numerically minimizing the potential  $V + \Delta V$  (in most cases with  $\Delta K_1 = 0$ ). We have used finite two-dimensional clusters of substrate atoms, allowing the atoms inside the cluster to relax but keeping the edges fixed, as outlined in Ref. [19]. We increased the size of the clusters until there was no appreciable change of the relaxation energies, which was usually about 10 layers of atoms around the chemisorbates. We have chosen the values of the effective force constants  $K_1$  and  $K$  of the substrate lattice so that a relaxation energy of around 1400 K and interaction energies, which are in agreement with low-coverage experimental data [10], are obtained, as shown in Table 1.

In order to obtain sufficiently large relaxation and interaction energies, we had to choose a small value for the force constant,  $K_1$ , between atoms in the first surface layer. (The value of  $K$  has little effect on the results.) The reduction from bulk values is characteristic of many closely packed noble-metal surfaces [27], but the reduction that

Table 1

Interaction energies  $W_{2NN}$  (in K) and the induced surface stress (in N/m) for on-top adsorption of CO on Pt(111)<sup>a</sup>

	$W_{2NN}$	$W_{3NN}$	$W_{4NN}$	$W_{5NN}$	$\tau$
Theory	194	314	108	119	1.24
Experiment	120 <sup>b</sup>	400 <sup>b</sup>	236 <sup>b</sup>		1.2 <sup>c</sup>

<sup>a</sup>  $W_{nNN} = 2E_0 - E_{nNN}$ , where  $E_0$  is the relaxation energy of a single CO molecule,  $E_{nNN}$  is the relaxation energy for two CO molecules adsorbed at the  $n$ th nearest-neighbour sites, etc. Theoretical values are calculated using  $K_1 = 4$  N/m,  $K = 2.5$  N/m,  $F_1 = 0.3 \times 10^{-9}$  N. The nearest-neighbour distance is  $a = 2.76$  Å.

<sup>b</sup> Ref. [10], low CO coverage.

<sup>c</sup> Ref. [21], CO coverage of 0.33.

we find is larger than that suggested in the surface phonon calculation in Ref. [28]. The large reduction may at least in part be a local effect, localized around the adsorption site, so that the derived value of  $K_1$  is not directly comparable with the lattice dynamics calculations. This point is further discussed in Section 5. The values in Table 1 show that the repulsive interaction is strong between adsorbates lying along closely packed chains of atoms and weaker for adsorbates separated by hollows, even if they are less far apart. In our opinion, the rather large interaction energy between fourth-nearest-neighbour adsorbates in Ref. [10] is influenced by the contributions from more distant sites, which were not included in their analysis. The smaller-than-expected value for second-nearest neighbours may be due to electronic effects.

Interaction energies have also been determined for CO chemisorbed on Rh [13,29] and Cu [12] surfaces. We discuss these systems only qualitatively, since the proposed values are less certain, and there are no quantitative data on other adsorbate-induced properties such as the induced surface stress. Wei et al. [13] estimated that  $W_2 = -100$  K and  $W_3 = 150$  K for the on-top chemisorbed CO on Rh(111). An earlier measurement by Payne et al. [29] reported  $W_2 = 170$  K and  $W_3 = -85$  K. In our model, the relative magnitudes of interaction energies for on-top adsorbates on fcc (111) surfaces are always similar to those found for CO/Pt(111). In particular, we expect a large repulsion between third nearest neighbour

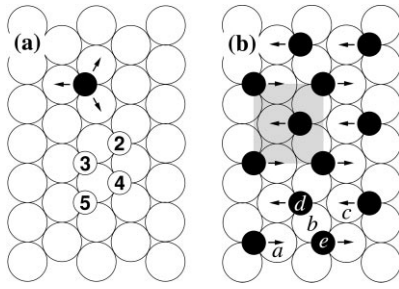


Fig. 2. (a) Chemisorption of CO (black circle) into a threefold hollow site on Ni(111). The relaxation of the adjacent Ni atoms is denoted by arrows. The numbers indicate possible adsorption sites of the same kind, either fcc or hcp. (b) Regular  $c(4 \times 4)$ -2CO structure on Ni(111) at a coverage  $\theta=0.5$ . An elementary cell (grey area) contains one adsorbate in the fcc and one in the hcp position,  $d$  and  $e$ . The relaxation of Ni atoms in intermediate rows,  $a$  and  $c$ , is denoted by arrows.

adsorbates, which lie along a chain of substrate atoms. In this respect, the values proposed in Ref. [13] seem more probable, although the origin of the attractive  $W_2$  (if it is real) is not clear. For the on-top CO on Cu(111), the same authors found  $W_2=107$  K,  $W_3>800$  K,  $W_4=155$  K [12]. The value of  $W_3$  seems too large compared with the other two, but otherwise, the results are quite similar to those for CO/Pt(111).

#### 4.3. Hollow-site adsorbates on (111) surfaces of fcc metals: CO on Ni

Clean nickel (111) surfaces do not reconstruct. Unlike several earlier claims, it has recently been accepted that, at low temperature, CO chemisorbs initially into threefold hollow sites [30,31], Fig. 2a. At room temperature, some bridge and on-top sites seem to be occupied even at low coverages [31]. At a coverage  $\theta=0.33$ , CO forms a regular  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure [32], but it is not clear whether the molecules adsorb into fcc or hcp positions. We describe the first layer of Ni atoms by the same potential as for Pt [Eq. (8)]. The interaction terms are similar to Eq. (9), but the adsorbate is in a threefold hollow site, and the sums run over the three surrounding Ni atoms. The induced surface stress is

$$\tau = -\frac{F_1}{a} \theta, \quad (11)$$

where the nearest-neighbour Ni–Ni distance is  $a=2.49$  Å. From the experimental data  $\tau=-0.55$  N/m at  $\theta=0.33$  [33], we obtain  $F_1=1 \times 10^{-10}$  N. We have estimated  $K_1=6$  N/m and  $K=2$  N/m from experimental data on the lateral displacement of the Ni atoms next to an adsorbate in a  $c(4 \times 2)$ -2CO structure, which forms at  $\theta=0.5$  [34], Fig. 2b. This is a considerable reduction from the bulk values, but not as large as for the Pt(111) surface, in agreement with the fact that the Ni(111) surface seems less prone to reconstruct than Pt(111). Using these parameter values, the relaxation energy for a single adsorbate is only 42 K, which is 30 times smaller than that found for CO/Pt(111). This leaves very little energy for adsorbate–adsorbate interactions, which turn out to be only a few K. In our opinion, the interaction energy of 100 K between second-neighbour adsorbates suggested by Skelton et al. [11] is either due to electronic mechanisms or is an artefact of the procedure. We note that an earlier study [35] reported that there was essentially no interaction already between second-neighbour adsorbates.

#### 4.4. Adsorbates on (100) surfaces of fcc metals: CO on Rh, Cu

The first atomic layer of a (100) surface of a fcc lattice has a square symmetry, and a central force between nearest neighbour atoms is not sufficient to ensure stability. The term that binds atoms to their respective equilibrium positions [ $K$  in Eq. (8)] stabilizes the structure, but some non-physical properties remain, e.g. the strain propagates only along the closely packed rows of atoms. The minimal model not affected by such problems has both the first- and the second-neighbour interaction:

$$V = \frac{1}{2} \sum_i \frac{1}{2} \left\{ \sum_{j=1}^4 K_1 [\hat{r}_{ij}(\mathbf{r}_i - \mathbf{r}_j)]^2 + \sum_{k=1}^4 K_2 [\hat{r}_{ik}(\mathbf{r}_i - \mathbf{r}_k)]^2 \right\} + \frac{1}{2} \sum_i K r_i^2, \quad (12)$$

where the index  $j$  runs over first neighbours and  $k$  over second neighbours around the site  $i$  (Fig. 3).



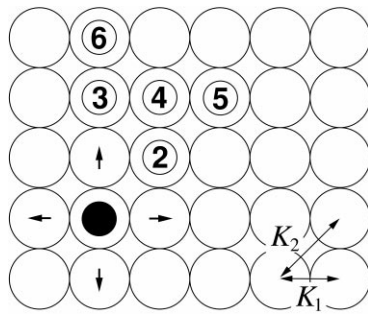


Fig. 3. Chemisorption of CO into on-top sites of a (100) surface of a fcc metal. Neighbouring chemisorption sites are denoted by numbers. In this work, we assume that in the first substrate layer, restoring forces exist between first neighbours, force constant  $K_1$ , and second neighbours, force constant  $K_2$ .

For chemisorption into on-top sites, the adsorbate-induced perturbation is

$$\Delta V = \sum_{j=1}^4 \frac{1}{2} \Delta K_1 [\hat{r}_{0j}(\mathbf{r}_0 - \mathbf{r}_j)]^2 - \sum_{j=1}^4 F_1 \hat{r}_{0j}(\mathbf{r}_0 - \mathbf{r}_j) + V'_0, \quad (13)$$

where we have assumed that only the first neighbours are affected.

Experimental data on adsorbate–adsorbate interaction energies exist for CO chemisorption on Rh(100),  $W_2=0$  and  $W_3=400$  K [13], and on Cu(100),  $W_2=-33$  K and  $W_3=13$  K [12]. No data on the induced surface stress are available for these systems. We have therefore used the values of the parameters  $K_1$  and  $K$ , which correspond roughly to a surface with little bond softening, and the values of  $F_1$  similar to those estimated for (111) surfaces, which is sufficient for a qualitative discussion. In Table 2 we show the calculated

Table 2

Interaction energies  $W_{nNN}$  (in K) for on-top adsorption of CO on fcc (100) surfaces, as a function of the strength of the second-neighbour interaction  $K_2$  (the values of other parameters are  $K_1=16$  N/m,  $K=5$  N/m,  $F_1=0.33 \times 10^{-9}$  N)

$K_2$ (N/m)	$W_{2NN}$	$W_{3NN}$	$W_{4NN}$	$W_{5NN}$	$W_{6NN}$	$-E_0$
0	0	193	0	0	112	579
4	-36	136	-14	9	57	388
8	-40	101	-15	13	33	302
16	-38	65	-13	14	15	214

values of  $E_0$  and  $W_{nNN}$ , for  $K_2$  varying between 0 and  $K_1$ . The interaction energies for adsorption sites along closely packed rows of atoms,  $W_{3NN}$  and  $W_{6NN}$ , are repulsive and decrease with increasing  $K_2$ . The interaction with the second-nearest-neighbour site is attractive for non-zero  $K_2$ , owing to the fact that the strain induced by the two adsorbates is largely collinear. These results are in good qualitative agreement with the experimental data cited earlier, i.e. there is a repulsion between third-nearest-neighbour adsorbates and possibly a weak interaction between second-nearest-neighbour adsorbates. This is a strong indication that in these systems, the substrate lattice relaxation is the dominant mechanism of the adsorbate–adsorbate interaction. We do not attempt to perform a quantitative analysis, since, at present, there are no data on the induced stress or other adsorbate-induced quantities, and the values of the interaction energies are uncertain. It is interesting that the continuum elastic theory [5] also gives a strong repulsion in the  $\langle 110 \rangle$  direction and possibly a weak attraction in the  $\langle 100 \rangle$  direction between adsorbates on (100) surfaces of noble metals. Recently, the interaction between N chemisorbed in the fourfold hollow sites on Fe(100) surface has been determined from high-resolution scanning tunneling microscopy images [36]. The interaction is attractive between second-nearest-neighbour adsorbates and weakly repulsive at larger distances. Ab-initio density functional theory calculations of this system presented in a subsequent publication [37] confirm that there are large lateral relaxations of Fe atoms around N chemisorbates. In order to analyse these results in terms of our model, the lattice dynamics of the surface layer should be re-evaluated, because the (100) surface of bcc Fe is considerably less dense than the closely packed fcc surfaces considered here.

## 5. Discussion

We have obtained good agreement for the adsorbate–adsorbate interaction energies and the surface stress for the on-top chemisorption of CO on Pt(111), which is the system for which the most reliable experimental data are available. Our

approach suggests that the interaction energies should scale similarly for on-top chemisorption on other (111) surfaces. This is consistent with available data, but experimental results appear less reliable. Qualitative agreement with experiment is also obtained for the chemisorption into threefold hollow sites on (111) surfaces (little or no interaction) and for on-top chemisorption on (100) surfaces (repulsion along rows of atoms).

The most serious quantitative problem is a small value of the force constant  $K_1$  between first neighbours in the first layer of Pt(111) deduced by comparison with experimental interaction energies. A small  $K_1$  is necessary in order to obtain sufficiently large interaction energies, since the other parameter in the model, the force  $F_1$ , is uniquely determined from the induced surface stress by using Eq. (10). The best first-principle calculations of the lattice dynamics of similar surfaces exist for Rh(111). In this case, the first-neighbour central force constant in the first layer is reduced by about a factor of two with respect to the bulk [38], but this is still much less than the reduction by almost an order of magnitude, which we have obtained. The tendency of the first layer of atoms on Pt(111) to reconstruct under some circumstances [22] indicates the softness of the force constant and possibly a large anharmonicity, but there is no other experimental or theoretical confirmation that the effect is so large. There are, however, other mechanisms that can lead to a large relaxation energy upon chemisorption and hence to a large adsorbate–adsorbate interaction, without affecting the induced surface stress. A strong coupling of the in-plane interatomic separation of the atom at the chemisorption site with the distance to the second layer has been found in the first-principle calculations of the lattice dynamics properties of the Rh(111) surface [38]. Also, the local change of the force constant around the adsorption site ( $\Delta K_1$  and similar terms in our notation) may contribute to a larger relaxation energy. Furthermore, the forces between the atom with the adsorbate and the neighbours in the second layer may be attractive, thus increasing the relaxation energy but decreasing the induced surface stress. More detailed experimental results, e.g. measurements of the atomic relaxation around the

adsorbate, and better first-principle calculations of the lattice dynamics of these surfaces would make it possible to determine more reliably the values of the dynamic matrix,  $D$ , and the chemisorption-induced forces,  $F$ . In turn, this will enable a more complete model to be constructed along the lines exposed in this paper, e.g. using a cluster that includes atoms in deeper layers and more realistic force constants.

The assumption that the adsorbate-induced forces superimpose linearly, condition (2) in Section 3, implies that, in our model, the chemisorption-induced stress depends linearly upon the coverage,  $\theta$ , if the force constants between the surrounding substrate atoms do not change upon chemisorption. The situation is more complex if there is a change, i.e. if the term  $\Delta K_1$  in Eq. (9) is not zero. As the adsorbate concentration becomes large, the regions with modified elastic properties around each adsorbate start to coalesce, and the elastic response of the entire first atomic layer changes. Experimental data [21] show that in most cases, the induced stress indeed depends linearly upon  $\theta$  at low coverages, with small deviations at larger  $\theta$  values, where the dependence usually becomes steeper. There are a few exceptions, which can be explained by changes in the adsorbate structure at certain adsorbate coverages. The most striking case is the chemisorption of CO on Ni(100) at room temperature, where the induced stress starts as tensile and depends linearly upon the coverage,  $\theta$ , but soon saturates and decreases, changing sign and becoming compressive at around  $\theta=0.2$ . The behaviour is not completely understood, and may be due to either chemisorption into two different sites with coverage-dependent probabilities or a strongly non-linear dependence of the character of the chemisorption bond upon the presence of other adsorbates in the neighbourhood. This behaviour is, however, quite exceptional, and an almost linear dependence on coverage is a rule.

## 6. Conclusions

The most important result of our calculation is the qualitative behaviour of the interaction energies:

- For on-top adsorption on (111) surfaces, e.g. Pt(111), the relaxation energy is large and the interaction repulsive and particularly strong along rows of atoms.
- For threefold hollow adsorption on (111) surfaces, e.g. Ni(111), the relaxation energy and, consequently, the interaction energies are small.
- For on-top adsorption on (100) surfaces, e.g. Rh or Cu, the interaction is repulsive along rows of atoms and can be weakly attractive between adsorbates across a hollow.

This agrees with experimental observations on CO chemisorption on these surfaces. In quantitative comparisons, we have also taken into account the magnitude of the adsorbate-induced surface stress, where available. Quantitative agreement is less certain, but improved models based on input from new experiments (adsorbate interaction energies, relaxation of substrate atoms) and from first-principle calculations of chemisorption could allow a rapid progress in that direction.

The fact that the relaxation energy on (111) surfaces is much larger for on-top than for hollow site adsorption means that first-principle calculations can give wrong ordering of the energy minima corresponding to different adsorption sites if full substrate relaxation is not taken into account.

To conclude, the qualitative agreement of the calculated and the measured adsorbate–adsorbate interaction energies of CO chemisorbed on several closely packed noble-metal surfaces strongly supports the phonon-mediated mechanism as the dominant contribution at intermediate adsorbate separations.

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