

Diffuse LEED theory from surfaces partially covered with molecules. II. Application to the case of the adsorption of CO on Pt(111)

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 1685

(<http://iopscience.iop.org/0953-8984/4/7/007>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 11/05/2010 at 00:02

Please note that [terms and conditions apply](#).

## Diffuse LEED theory from surfaces partially covered with molecules: II. Application to the case of the adsorption of CO on Pt(111)

J C Le Bossé†‡, J Lopez†‡, J Rousseau†‡ and I Zasada†‡§

† Laboratoire de Tribologie et de Dynamique des Systèmes CNRS-URA 855, Ecole Centrale de Lyon, 36 Avenue Guy de Collongue, BP 163 69 131, Ecully, France

‡ Ecole Nationale d'Ingénieurs de St Etienne, 58 rue Jean Parot, 42025, St Etienne, France

Received 17 April 1991, in final form 7 June 1991

**Abstract.** The aim of this paper is to investigate the relative influence of geometrical and order parameters on diffuse LEED intensities. In most diffuse LEED studies relative to molecules adsorbed at single crystal surfaces, there are probably several chemisorption sites or several adsorbed species. For this reason, this situation is examined in detail here. The elastic diffuse LEED intensity from a single crystal surface Pt(111) partially covered with CO molecules is calculated for different values of the parameters which characterize the adsorbate/substrate model. These parameters are separated into: geometrical parameters related to the local arrangement of atoms near chemisorption sites, and order parameters related to the statistical distribution of the occupied chemisorption sites. In the present case, the geometrical parameters are the C–Pt and the C–O bond lengths and the location in the 2D unit cell of the surface lattice (bridge and top sites). The order parameters are the site occupancy pair correlation functions or the quantities which determine them: surface coverage, surface temperature, pair interaction potential between adsorbates, etc. Even in the case of a short-range order, the sensitivities of diffuse intensities to both kinds of parameters are found very similar. On the other hand, in the situation where several kinds of chemisorption sites exist, the diffuse LEED intensity is not the product of a form factor and a structure factor. So the use of the Y function method, which avoids the structure factor determination, is not possible. Thus, a determination of the statistical distribution of adsorbates at the substrate surface cannot be circumvented.

### 1. Introduction

In two previous papers (Le Bossé *et al* 1988, 1990), we have developed a general theory of diffuse LEED at an ordered single-crystal surface partially covered with a disordered layer of molecules. According to this theory, the relative diffuse LEED intensity per unit of solid angle is expressed in terms of:

(i) the renormalized transition matrices  $K_1(p)$ , one for each of the adsorbed species, denoted by  $p$ ;

(ii) the structure factors  $S(p, p')$  which are the Fourier transforms of the site occupancy pair correlation functions.

§ Permanent address: Institute of Physics, Łódź University, 90–236 Łódź, Poland.

Let us first examine in detail the simplest case where there is only one adsorbed species. In this case, the expression of the diffuse LEED intensity reduces to the product of a form factor  $|K_1|^2$  by a structure factor. Saldin *et al* (1985) had previously derived this result from a more succinct approach. Moreover, starting from this particular expression and noting that the structure factor  $S$  only depends on the difference  $\Delta k_{\parallel}$  between the parallel components of the initial and final wave vectors, they introduced the logarithmic derivative  $L$  of the diffuse intensity with respect to energy at constant  $\Delta k_{\parallel}$ , which only depends on the form factor. In order to eliminate the singularities of  $L$ , they made use of a function denoted by  $Y$ , depending on  $L$ , and on the adsorption potential  $V_i$ .  $Y$  and  $L$  are related to the local atomic configuration near a chemisorption site and are independent of the statistical distribution of occupied chemisorption sites. So, the diffuse LEED technique associated with the  $Y$  function method seems well suited to the determination of short-range structural information and easy to use since it avoids any structure factor determination.

Let us now examine more complex situations in which either several species are adsorbed or only one species is located at several kinds of chemisorption sites. Then, the expression of the diffuse LEED intensity is no longer a simple product of two factors† and, for this reason, the use of the  $Y$  function becomes deeply questionable. Two different situations must be examined.

(i) The occupied chemisorption sites are randomly distributed at the surface. In this case, the structure factors reduce to self-correlation functions independent of the wave-vector. Neglecting interference between the renormalized transition matrices  $K_1(p)$ , the diffuse intensity is approximately a sum of the form factors  $|K_1(p)|^2$  weighted by the partial average occupancies of states  $p$ . So, in the absence of a short-range order, the  $Y$  function method is useless since diffuse intensities only depend on form factors and, thus, no structure factor has to be eliminated. In fact, in the present case, the use of this method amounts to a comparison of the calculated and experimental diffuse intensities through a particular function of both of them.

(ii) The occupancies of chemisorption sites are correlated and now the structure factors no longer reduce to self-correlation functions independent of the wave-vector. As previously seen, in such cases the determination of these structure factors cannot be avoided by the use of the  $Y$  function method. However, this method has been used in some situations where the existence of a short-range order is suspected (Saldin *et al* 1985, Starke *et al* 1988). So, the introduction of a short-range order either causes a negligible change in intensities, and the elimination of a negligible structure factor holds no interest (situation similar to the previous one); or causes a change comparable to the one induced by a noticeable modification of the geometrical parameters, and consequently the structure factors have to be determined.

To clarify this point, in this paper we shall examine the relative sensitivity of diffuse LEED intensities to the order parameters and to the geometrical parameters.

For this purpose, we have chosen the case of the adsorption of CO on the Pt(111) surface because this system has been the subject of many studies (Steininger *et al* 1982, Ogletree *et al* 1986, Blackman *et al* 1988). Presently, our aim is not to compare experiment and theory, but to examine carefully, in this particular case, the relative importance of

† As a matter of fact it is expressed as a quadratic form of the effective scattering amplitudes of the adsorbates. The coefficients of this quadratic form are related to the structure factors (Le Bossé *et al* 1988).

the parameters that characterize the location of the atoms surrounding a chemisorption site and the parameters that characterize the statistical distribution of the occupied sites.

In our diffuse LEED theory, the form factors are expressed in terms of the transition matrix of the admolecule. In Part I of this work, we developed a theory of multiple scattering within a molecule, from which we can draw a usable expression of this transition matrix. So, it is now possible to investigate numerically the particular situation of CO adsorbed on Pt(111). Calculation of diffuse LEED intensities requires the use of five computer programs.

(i) The first one allows calculation of the elements of the carbon monoxide transition matrix in the basis of free spherical waves.

(ii) The second one provides the scattering amplitudes of the Pt(111) single-crystal surface.

(iii) The renormalized transition matrix of the molecule in the presence of the substrate is calculated from the third one, in which the input data are the output data of both previous programs.

(iv) The site occupancy pair correlation functions and the structure factors are calculated in the fourth program.

(v) The last program provides the diffuse-LEED intensities

Some further details of the methods and approximations used are given in section 2. Results of the numerical application are then shown and discussed in section 3.

## 2. Calculation of diffuse LEED spectra from CO/Pt(111)

### 2.1. Calculation of the CO transition matrix

This computation is based upon the multiple scattering theory of electrons at a single molecule, as developed in Part I. Let us recall that calculations are carried out for an incident beam energy of 60 eV and that the potentials at the side of the muffin-tin spheres of carbon and oxygen are assumed to be equal to platinum's potential. This leads us to consider that the carbon monoxide molecule is immersed in an homogeneous medium whose potential is the platinum optical potential  $V_{\text{opt}}$ . At 60 eV,  $V_{\text{opt}} = -12.499 - 4.013i$  eV (Rundgren, private communication) and thus, the energy of the incident electrons with respect to the muffin-tin zero energy of carbon and oxygen is 72.499 eV. According to Ogletree *et al* (1986) we shall consider some values of the CO bond length near 1.15 Å. As the CO bond is normal to the surface, it is orientated along the incident beam direction which is also the  $z$  axis direction. The CO transition matrix elements depend upon the choice of the origin of the space: we choose it to be at the centre of the CO bond.

In Part I, it was shown that, for this incident energy and for a CO bond length of 1.15 Å:

(i) the size of the molecule is such that the transition matrix elements corresponding to  $l > 6$  can be neglected;

(ii) multiple scattering effects inside the CO molecules play an important role;

(iii) the transition matrix of CO is a square matrix of order 98 in which most of the elements are zero, due to the axial symmetry of the beam-molecule system.

These results remain valid when the CO bond length varies by  $\pm 0.1$  Å.

## 2.2. Computation of the scattering amplitude of the Pt(111) surface

At 60 eV, this computation only requires the use of the six first phase shifts of platinum. Then, one needs to determine:

(i) the first column of the scattering amplitude matrix  $M_s$  computed for  $k_{\parallel} = 0$  (normal incidence). As the LEED wave function is represented by a convergent Fourier series, only  $N_f$  of its matrix elements  $M_s(k_{\parallel}^- \leftarrow k_{\parallel}^+)$ , labelled with the reciprocal vectors  $g$ , are kept;

(ii) the first line of scattering matrices  $M_s(k_{\parallel}^- \leftarrow k_{\parallel}^+)$  computed for wave-vectors  $k_{\parallel}$  corresponding to each of the scattering directions  $(\theta_f, \varphi_f)$  considered. As previously, only  $N_f$  Fourier components of the LEED wave are kept.

At 60 eV, convergence of the matrix elements is obtained for  $N_f = 32$ . On the other hand  $N_f$  which depends on  $(\theta_f, \varphi_f)$  varies from 30 to 35. Except for the truncation of the Fourier series,  $M_s$  is obtained from exact calculation methods: the Bloch wave method (McRae 1968) for interplanar scattering; and Kambe's method (Kambe 1967a, b, 1968) for planar scattering.

Diffuse LEED intensity maps have been plotted from a set of 697 scattering directions corresponding to the 697 vectors  $k_{\parallel}$  whose components are chosen in the following way:  $k_{fx} = n\Delta k$ ,  $k_{fy} = m\Delta k$ ,  $n$  and  $m$  are integers,  $m$  is positive,  $\theta_f < \theta_{\max} = 60^\circ$ . Let us point out that computation of scattering amplitudes from the Pt(111) surface is by far the most time consuming.

## 2.3. Renormalized transition matrix of the molecule and diffuse LEED intensities for CO on Pt(111)

The renormalized transition matrix  $K_1(p, k_{\parallel}^- \leftarrow k_{\parallel}^+)$  of the CO molecule is simply evaluated by using expression (3a) given in Le Bossé et al (1990). Let us notice that the maximum value  $p_{\max}$  of  $p$  may be 1 for the case where CO is adsorbed at the on-top sites only, 3 for the case of bridge sites only and 4 when CO can be adsorbed at both kinds of sites. By computing separately the effective transition matrix, the C-Pt bond length or the chemisorption site can be changed without having to compute again the platinum scattering amplitudes or the CO transition matrix.

Computation of diffuse-LEED intensities from expression (1) given in the paper mentioned above, requires the determination of the structure factors  $S(p, p', k_{\parallel} - k_{\parallel})$ . In the present work, the sensitivity of diffuse LEED intensities to a local order inside the adsorbed layer is investigated in the case of binary chemisorption (adsorption of CO at top sites only,  $p_{\max} = 1$ ). In this case, the expression  $S(1, 1, k_{\parallel} - k_{\parallel}) = F(k_{\parallel} - k_{\parallel})$  is obtained from a self-consistent molecular field approximation of the site-occupancy pair correlation function (Le Bossé et al 1990).

## 2.4. Structure factor and site occupancy pair correlation function

The previous expression of  $F(k_{\parallel} - k_{\parallel})$  must always be used at low coverage in the situations where adsorbates interact by a short-range repulsive potential; or adsorbates interact by a short-range attractive potential that is small compared with  $\beta = kT$  ( $k$  is the Boltzmann constant and  $T$  the surface temperature).

In the case of a surface square lattice, we have shown that the structure factor can be directly calculated without a preliminary determination of the pair correlation function

(Le Bossé *et al* 1990). Similar work can be done in the present case of a triangular lattice. So, denoting  $k_{\parallel} - k_{\parallel}$  by  $q$ , the equations to solve reduce to

$$F(q) = \theta(1 - \theta)/[1 + \beta\theta(1 - \theta)U^*(q)] \quad (1a)$$

$$U^*(q) = 2U^*[\cos(q_x a\sqrt{2}/2) + 2\cos(q_x a\sqrt{2}/4)\cos(q_y a\sqrt{6}/4)] \quad (1b)$$

$$U^* = U(1 + \gamma_{10}/\theta^2) \quad (1c)$$

$$\gamma_{10} = a^2 \frac{\sqrt{3}}{8\pi^2} \iint_{B_1} d^2q F(q) \cos\left(q_x a \frac{\sqrt{2}}{2}\right). \quad (1d)$$

In these relations  $\theta$  is the surface coverage in CO molecules, which is generally fixed in diffuse LEED experiments;  $a$  is the unit cell parameter of the face-centred cubic lattice of platinum ( $a = 3.9237 \text{ \AA}$ );  $U$  is a potential which describes the interaction between CO molecules adsorbed at adjacent sites;  $U^*$  is the effective pair interaction potential which takes into account correlations between the average occupations of sites  $i$  and  $j$  for which  $U_{ij} \neq 0$  (Le Bossé *et al* 1990); and  $\gamma_{10}$  is the nearest-neighbour site occupancy pair correlation function.

A self-consistent solution of (1a – d) is obtained by using the following process. An initial value of  $U^*$  is chosen. So, using (1a) and (1b), a calculation of the structure factor  $F(q)$  is carried out. From this estimation of  $F(q)$  and the use of relation (1d), a value of the correlation function  $\gamma_{10}$  is determined. Finally, using this value of  $\gamma_{10}$  in expression (1c), a new estimate of  $U^*$  can be obtained. This process is repeated until the initial and final values of  $U^*$  coincide. Let us note that the Fourier transform in (1d) is an integral over the first Brillouin zone  $B_1$  of the triangular surface lattice.

### 3. Results

In all subsequent situations, it is assumed that:

- (i) platinum atoms which surround occupied and unoccupied chemisorption sites have the same location (absence of induced relaxation);
- (ii) C–O and C–Pt bonds remain perpendicular to the surface.

So, with these assumptions, diffuse LEED intensities *a priori* depend on:

- (a) the spatial arrangement of the carbon and oxygen atoms relative to the platinum surface atoms;
- (b) the statistical distribution of the occupied chemisorption sites at the surface.

In the first stage, we shall only consider the sensitivity of diffuse LEED intensities to geometrical parameters. In the present case, these parameters are the location in space of carbon and oxygen adatoms. In this way, other parameters have to be fixed: CO molecules are assumed to be randomly distributed at 15% of either of both considered sites (either on-top or bridge sites).

In the second stage, we shall examine the sensitivity of diffuse intensities to the presence of a short-range order inside the adsorbed layer. Now, geometrical parameters have to be fixed: chemisorption at the on-top sites only is considered and the interatomic distances between C and O and between C and Pt are those commonly found in the literature (Ogletree *et al* 1986, Blackman *et al* 1988).

### 3.1. Definition of a set of reference values for parameters

In the first stage, where the CO molecules are randomly distributed at one kind of site, it has been shown that the relative diffuse LEED intensity per unit of solid angle is given by (Le Bossé *et al* 1988, 1990)

$$I(k_{\parallel} \leftarrow k_{\parallel}) = (4\pi^4 k k_{\perp}^2 / A k_{\perp} |K_{\perp}|^2) \theta(1 - \theta) |K_{\parallel}(k_{\parallel} \leftarrow k_{\parallel})|^2. \quad (2)$$

Sensitivities to bond lengths are investigated by varying the C–Pt and the C–O bond lengths from the values given by Ogletree *et al* (1986), that is to say: 1.85 Å for C–Pt and 1.15 Å for C–O. For this set of reference values, diffuse LEED intensities are computed and their values are plotted in figures 1(a) and 1(b). Figure 1(b) clearly shows a three-fold axis of symmetry. However, we have to note that the symmetry of this map is very close to hexagonal symmetry, that is to say the one of a surface atomic layer. This only indicates that the greatest number of atoms which participate in incoherent scattering of electrons are those belonging to the surface atomic layer. Full circles appearing in figure 1(b) represent the position of the 10, 01,  $\bar{1}1$  and  $\bar{1}0$  diffraction spots. Note that these spots approximately coincide with four smooth peaks whose heights are about 0.015 and 0.0125. Three full triangles represent the three fractional spots  $\frac{1}{3}\frac{1}{3}$ ,  $\frac{2}{3}\frac{2}{3}$  and  $\frac{2}{3}\frac{1}{3}$  associated with the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  superstructure. They also approximately coincide with three smooth peaks whose height is 0.0125 sterad<sup>-1</sup>.

### 3.2. Comparison of intensities

Diffuse LEED intensities obtained for different interatomic distances are compared by using the distance:

$$d(I_1, I_2) = \left[ \iint_{\mathcal{D}} |\mathcal{F}_1(k_{\parallel} \leftarrow k_{\parallel}) - \mathcal{F}_2(k_{\parallel} \leftarrow k_{\parallel})|^2 d^2 k_{\parallel} \right]^{1/2} \quad (3a)$$

between normalized intensities defined by:

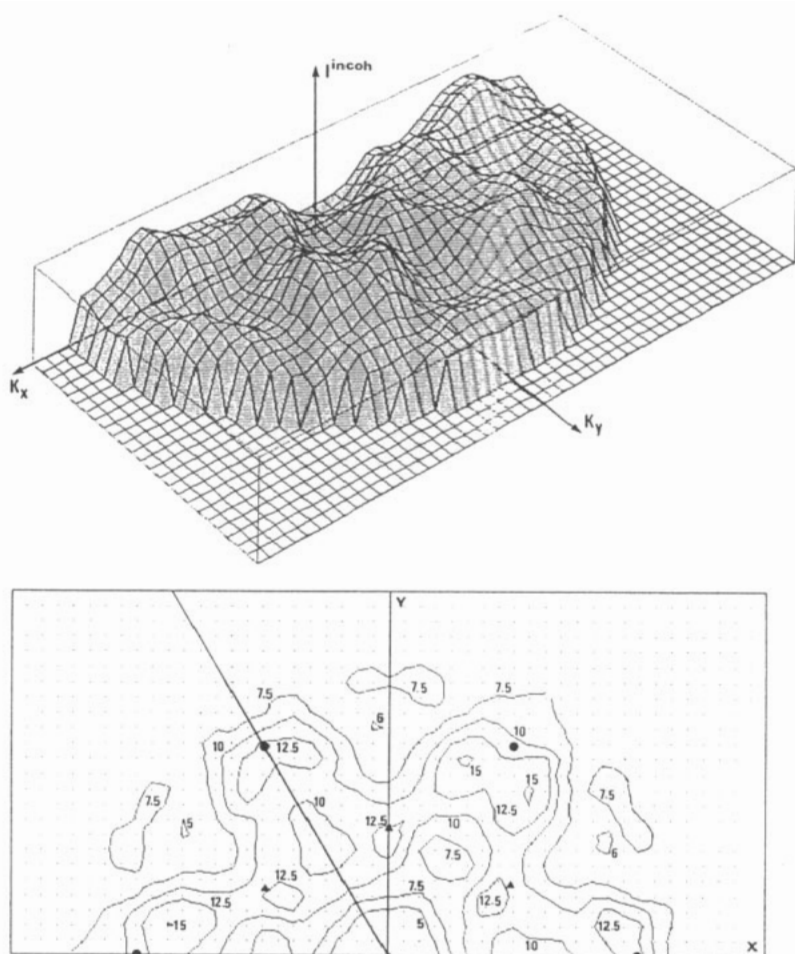
$$\mathcal{F}_1(k_{\parallel} \leftarrow k_{\parallel}) = I_1(k_{\parallel} \leftarrow k_{\parallel}) / \left[ \iint_{\mathcal{D}} |I_1(k_{\parallel} \leftarrow k_{\parallel})|^2 d^2 k_{\parallel} \right]^{1/2}. \quad (3b)$$

In these relations, the integration is performed over the domain  $\mathcal{D}$  of the reciprocal space where the diffuse LEED intensities are calculated ( $\theta_f < 60^\circ$ ). By using this method of comparison, intensities which differ in a multiplicative factor are considered to be identical. On the other hand, differences in locations or in the relative heights of structures such as peaks, valleys, saddle points, are taken into account.

### 3.3. Sensitivity to the geometrical parameters

**3.3.1. Sensitivity to the C–O and C–Pt bond lengths.** Variations of  $\pm 0.05$  Å and  $\pm 0.1$  Å from their reference values are examined. Results of this study are summarized in table 1.

Different values of the C–O bond length are tried from 1.05 Å to 1.25 Å while the C–Pt bond length is kept equal to its reference value. Let us remark that increasing the C–O bond length from 1.15 Å to 1.25 Å induces a larger change in diffuse intensities than decreasing from 1.15 to 1.05 Å. A similar trend is observed when the CO molecule is displaced from 1.85 Å to 1.95 Å and from 1.85 Å to 1.75 Å. Moreover, a variation of the C–Pt bond length induces a larger change in intensity than the same variation of the

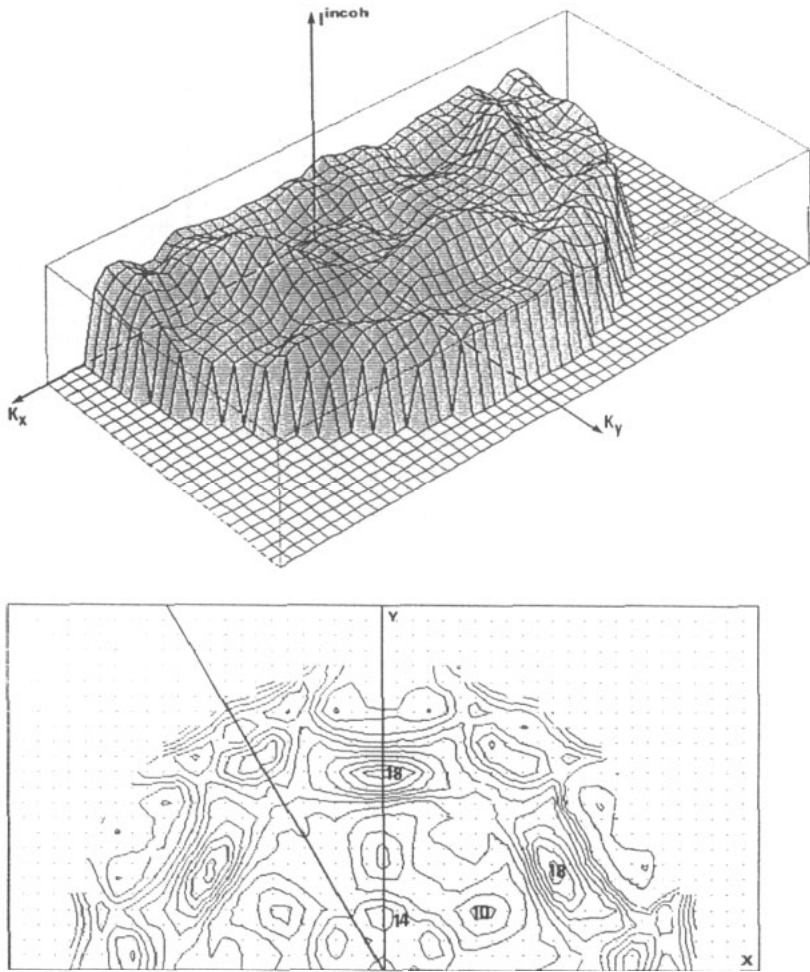


**Figure 1.** Elastic diffuse LEED intensities for CO/Pt(111), an energy of 60 eV with the incident beam normal to the surface. The intensity maps are computed for the following values of parameters: distance C–O = 1.15 Å; distance C–Pt = 1.85 Å; on-top sites; coverage  $\theta = 15\%$ ; random distribution of occupied sites. (a) Perspective graphical representation. (b) Contour plot representation with values of intensities going from 5 to 15 in steps of 2.5 (5 corresponds to a relative intensity of 0.005 per unit of solid angle).

**Table 1.** Variation of C–O and C–Pt bond lengths.

C–Pt bond length = 1.85 Å		C–O bond length = 1.15 Å	
C–O bond length (Å)	$d(I_1, I_2)$	C–Pt bond length (Å)	$d(I_1, I_2)$
1.05	0.138	1.75	0.206
1.10	0.076	1.80	0.115
1.15	0.000	1.85	0.000
1.20	0.097	1.90	0.134
1.25	0.222	1.95	0.266





**Figure 2.** Same as in figure 1 except that the distance C–Pt = 1.55 Å and the chemisorption sites are three kinds of bridge sites occupied with 5% of CO molecules.

C–O bond length. This comes from the fact that in the first case two scatterers are displaced whereas only one scatterer is displaced in the second case. Actually, the main point we have to keep in mind is that the sensitivities of diffuse intensity to both geometrical parameters are comparable.

**3.3.2. Sensitivity to the geometry of the chemisorption site.** Let us now consider the case where the CO molecules are adsorbed at the bridge sites. According to Ogletree *et al* (1986), the distance from the carbon atom to the top layer of platinum is chosen to be equal to 1.55 Å. Now, due to the fact that the Pt(111) surface has a three-fold axis of symmetry, three kinds of equivalent bridge sites have to be considered ( $p_{\max} = 3$ ). Moreover, these three bridge sites are assumed to be randomly occupied with the same average occupation, that is to say 5%. In this way, expression (2) of the diffuse LEED

intensity, only valid for  $p_{\max} = 1$ , can no longer be used. It is therefore necessary to return to the general expression of the diffuse LEED intensity (Le Bossé *et al* 1990). In the present case, it reduces to:

$$I(k_{\parallel} \leftarrow k_{\parallel}) = (4\pi^4 k_{\perp}^2 / A k_{\perp} |K_{\perp}|^2) \left[ (\theta/3)(1 - \theta/3) \sum_{p=1}^3 |K_1(p, k_{\parallel} \leftarrow k_{\parallel})|^2 - \frac{2\theta^2}{9} \text{Real} \sum_{\substack{p < p' \\ 1}}^3 \overline{K_1(p, k_{\parallel} \leftarrow k_{\parallel})} K_1(p', k_{\parallel} \leftarrow k_{\parallel}) \right]. \quad (4)$$

Figures 2(a) and 2(b) show the map intensity obtained for bridge-sites. Figure 2(b) indicates that, similar to the case of top-sites, the symmetry of this map is very close to hexagonal symmetry although it is actually three-fold symmetry. Nevertheless, this is the only common feature between both cases. We observe three smooth peaks whose height is about  $0.018 \text{ rad}^{-1}$ , but contrary to the case of top-site the peaks do not coincide with the diffraction spots. Moreover, the intensity maxima which were observed near the fractional diffraction spots are replaced now with relative intensity minima (height about  $0.010 \text{ rad}^{-1}$ ). So, in the present case, we can think that the features of the spectra shown in figures 1 and 2 are so different that a simple visual examination allows discrimination of both kinds of site. Unfortunately, it would seem that in the actual situation there is a mixture of top and bridge sites (Blackman *et al* 1988).

Let us call  $I_t$  and  $I_b$  the diffuse LEED intensities obtained for top and bridge sites. The distance between these intensities is  $d(I_t, I_b) = 0.326$ , that is to say about twice the distances obtained for a variation of 8% of C–O or C–Pt bond lengths. Consequently, sensitivities of spectra to the displacement of CO from one site to the other are not very different from the sensitivity to bond length variations. It can be thought, then, that chemisorption site and bond length changes induce comparable variations of the distance defined by (3a) between experiment and theory.

*3.3.3. Remark about the case of a mixture of several chemisorption sites.* It has been assumed that the total diffuse LEED intensity is a linear combination  $\theta_1 I_1 + \theta_2 I_2 + \theta_3 I_3$  of diffuse LEED intensities  $I_1, I_2$  and  $I_3$  associated with chemisorption sites 1, 2 and 3 for which partial coverages are  $\theta_1, \theta_2$  and  $\theta_3$  respectively (Blackman *et al* 1988). Obviously, such an assumption totally excludes the possibility that site occupancies are correlated. However, even in this case, expression (4) of the diffuse intensity shows that this assumption is only valid in the limit of low coverages. In the present particular case where  $\theta = 15\%$ , the diffuse intensities obtained by neglecting the interference terms of (4) and by replacing  $\theta - \theta^2$  with  $\theta$  are close to those obtained from the exact expression. More precisely, the distance between both normalized intensities is only 0.0103 and the height of the three smooth peaks appearing in the approximated relative intensity map is 0.022 instead of  $0.018 \text{ sterad}^{-1}$  for the exact one (see figure 2(b)). Examination of table 1 indicates that such a distance between intensities may correspond to variations of  $0.01 \text{ \AA}$  of the C–Pt bond length. So, interference terms which vary as  $\theta^2$  can be legitimately suspected to play a non-negligible role when coverage  $\theta$  is between 20 and 30%†. As a matter of fact, the possibility of measuring an electron current outside the diffracted beam directions (i.e. a diffuse LEED current), which is substantially issued

† Nevertheless, for such coverages, correlations between neighbour site occupancies are probably important, and consequently the expression is no more correct.

from the disorder of the overlayer and not from the disorder of the substrate due to steps, vacancies, missing rows, etc, requires dealing with a sufficiently large coverage  $\theta$ . So, in such a situation, it would be wise to compare theory to experiment by keeping the interference terms.

### 3.4. Sensitivity to a short-range order

Let us now consider a distribution of molecules adsorbed at top sites. The C-Pt and C-O distances are fixed to the reference values. The coupling between molecules is assumed to be a nearest-neighbour pair interaction potential. If this coupling is strong enough, site occupancies are correlated and the diffuse LEED intensity is given by (Le Bossé et al 1990):

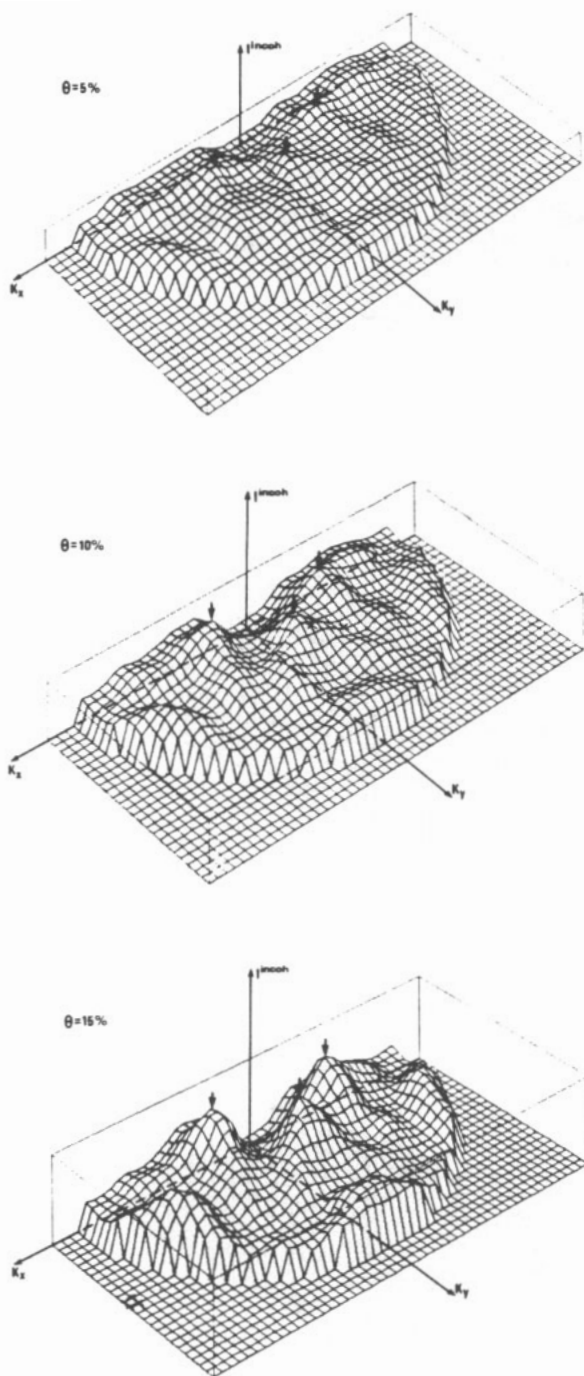
$$I(k_{\parallel} \leftarrow k_{\parallel}) = (4\pi^4 k k_{\perp}^2 / Ak_{\perp} |K_{\perp}|^2) F(k_{\parallel} - k_{\parallel}) |K_{\perp}(k_{\parallel} \leftarrow k_{\parallel})|^2. \quad (5)$$

Resolution of  $(1a-d)$  leads to the structure factor  $F(k_{\parallel} - k_{\parallel})$ . These equations indicate that the existence of a local order inside the overlayer is determined by the dimensionless ratio  $\beta U$  and the coverage  $\theta$ . As previously mentioned,  $(1a-d)$  can only be used at low coverage, for any value  $U$  in the case of repulsive coupling and for weak values of  $U$  in the case of attractive coupling.

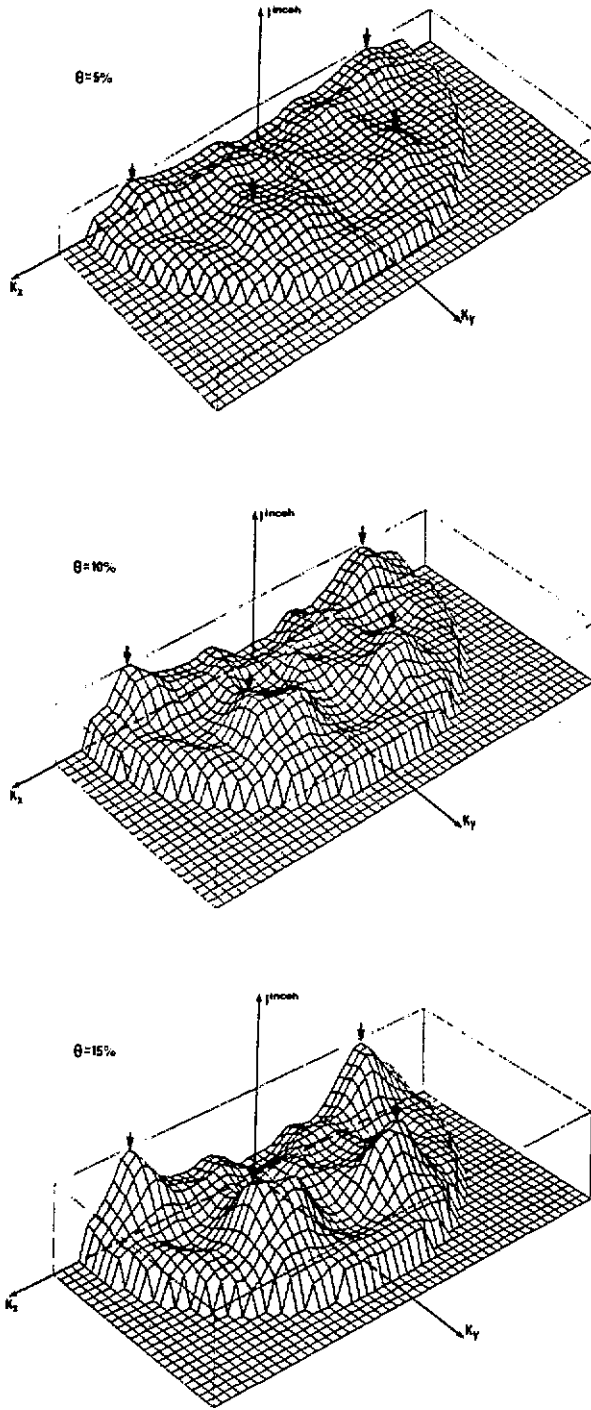
**3.4.1. Case of a repulsive interaction potential.** The case of a repulsive interaction between admolecules is illustrated with  $\beta U = 4$ , for different values of  $\theta$ : 5%, 10% and 15%. For these three coverages, (1) leads to the effective interaction potentials  $\beta U^*$ : 0.6609, 0.92041 and 1.04188 respectively. For each of these values, first the structure factor is determined, then the diffuse LEED intensities can be calculated. Results of these calculations are illustrated in figure 3.

Firstly, let us note that the diffuse intensities increase with the coverage in CO molecules, which is an obvious result because incoherence of back-scattered waves comes from the presence of these molecules. For  $\theta = 5\%$ , the distance between normalized spectra obtained for a random distribution of molecules (case  $\beta U = 0$ ) and for  $\beta U = 4$  is 0.079. By doing a similar comparison for  $\theta = 15\%$ , the distance between both spectra becomes 0.313. So, as could be expected, the local order strongly increases with surface coverage  $\theta$ . Examination of figure 3 clearly shows that an increase in  $\theta$  induces a fast growing of the peaks located near the fractional diffraction spots  $\frac{1}{3}\bar{1}$ ,  $\frac{2}{3}\bar{1}$  and  $\frac{2}{3}\bar{2}$  (marked by arrows). This indicates a trend to the appearance of a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  superstructure where an occupied site is surrounded by six unoccupied sites. This result is in accordance with the short-range order which can be expected in the case of a strong repulsive potential.

**3.4.2. Case of an attractive interaction potential.** In this case, the structure factor is directly obtained by replacing  $U^*$  with  $U$  in  $(1a)$ . Calculations are carried out in the case  $\beta U = -0.5$  and values 5%, 10% and 15% of  $\theta$  are tried again. As previously, for a surface coverage of 5%, the distance between the normalized spectra obtained for  $\beta U = -0.5$  and for  $\beta U = 0$  is small (0.066) compared with the distance between both similar spectra calculated for  $\theta = 15\%$  (0.201). So, as in the case of a repulsive interaction, a local order increasingly appears for larger and larger surface coverages. Figure 4 shows that the four peaks located near the  $10$ ,  $01$ ,  $\bar{1}1$  and  $\bar{1}0$  diffraction spots (marked by arrows) increase with  $\theta$ . This indicates a trend to the appearance of a  $1 \times 1$  structure in the adlayer where an occupied site is surrounded by six occupied sites. This trend to a



**Figure 3.** Diffuse LEED intensities obtained in the same condition as in figure 1 except that top sites are not randomly occupied. Now, it is assumed that molecules adsorbed at adjacent sites interact by a repulsive potential of  $4kT$ . When coverage  $\theta$  increases, three peaks become sharper and sharper in the vicinity of the fractional spots associated with the  $\sqrt{3} \times \sqrt{3}R30$  superstructure.



**Figure 4.** Same as in figure 3 except that adjacent admolecules interact by an attractive potential  $-0.5 kT$ . Now, when  $\theta$  increases, the presence of this potential causes the progressive appearance of four peaks located near the first integer spots associated with the  $1 \times 1$  structure.

local condensation of CO molecules is consistent with the attractive behaviour of the interaction between molecules.

#### 4. Summary and conclusion

In this paper, we have examined the sensitivity of diffuse LEED intensities to geometrical and order parameters. For this purpose, a reference situation has been preliminarily defined: adsorption at the on-top sites, coverage  $\theta = 15\%$ , random distribution of occupied sites,  $d(\text{C-O}) = 1.15 \text{ \AA}$  and  $d(\text{C-Pt}) = 1.85 \text{ \AA}$ . Then, the change in intensity induced by a variation of each of these parameters from its reference value has been calculated. This change is quantitatively characterized by a distance between normalized spectra. So, the following variations have been obtained.

0.138 when the C-O bond length goes from  $1.15 \text{ \AA}$  to  $1.05 \text{ \AA}$ ;

0.206 when the C-Pt bond length goes from  $1.85 \text{ \AA}$  to  $1.75 \text{ \AA}$ ;

0.326 when CO is displaced from on-top sites to bridge sites (the distance from C to the top layer of platinum becomes  $1.55 \text{ \AA}$ );

0.313 when a short-range repulsive potential  $4kT$  between CO admolecules is introduced;

0.201 when a short-range attractive potential  $-0.5 kT$  is introduced.

Let us first remark that all of these changes in intensities have the same order of magnitude. Let us also point out that the order inside the overlayer has a range which does not exceed one or two interatomic distances. Consequently, it is unreasonable to compare experiment and theory without taking account of all geometrical and order parameters.

However, in the particular case where one adsorbate is chemisorbed at one kind of site, the general expression of the diffuse LEED intensity (Le Bossé *et al* 1990) reduces to (5). With this particular expression, the  $Y$  function method allows calculation of a quantity which only depends on the form factor (Heinz *et al* 1985, Saldin *et al* 1985)

$$(4\pi^4 k k_{f\perp}^2 / Ak_{i\perp} |K_{f\perp}|^2) |K_1(\mathbf{k}_{\parallel} \leftarrow \mathbf{k}_{\parallel})|^2.$$

The main interest of this method is to avoid the calculation of the structure factor  $F(\mathbf{k}_{\parallel} - \mathbf{k}_{\parallel})$ .

On the other hand, the  $Y$  function method cannot be applied in the case where several chemisorption sites or several adsorbates exist. Then, measured and calculated intensities must be directly compared. Consequently, we are in one of the two following situations.

(i) Coverage is low and there is no correlation between occupancies of neighbouring sites. Then, the intensity can be approximated as a quadratic form of the form factors associated with each of the chemisorption states. In the limit of very low coverages, this quadratic form becomes diagonal and the coefficients are the partial coverages of each chemisorption state. In fact, the expression of diffuse LEED intensities does not depend on a structure factor and thus the problem of its determination does not have to be taken into consideration. Thus, the use of the  $Y$  function method would have no sense in this case.

(ii) Coverage is low, but occupancies of adjacent sites are correlated. Now, the expression of the diffuse intensity depends on a structure factor whose importance has

been examined in the particular case of binary chemisorption. It has been established that variations of intensity induced by introducing a short range order are comparable to those induced by a non-negligible change in geometrical parameters. It can be thought that this conclusion remains valid in the case where several kinds of chemisorption sites exist. Thus, the reliability of interatomic distances (or of other parameters such as coverage) can be considered as doubtful when they are drawn from a comparison between experiment and a theory which neglects this structure factor.

## References

- Blackman G S, Xu M L, Ogletree D F, Van Hove M A and Somorjai G A 1988 *Phys. Rev. Lett.* **61** 2352-5  
Heinz K, Saldin D K and Pendry J B 1985 *Phys. Rev. Lett.* **55** 1312-5  
Kambe K 1967a *Z. Naturf.* a **22** 322-30; 1967b *Z. Naturf.* b **22** 422-31; 1968 *Z. Naturf.* a **23** 1280-94  
Le Bossé J C, Lopez J, Rousseau J and Zasada I 1988 *J. Phys. C: Solid State Phys.* **21** 565-88  
Le Bossé J C, Lopez J, Rousseau J, Zasada I and Wojtczak L 1990 *J. Phys. Condens. Matter* **2** 3143-65  
McRae E G 1968 *Surf. Sci.* **11** 479  
Ogletree D F, Van Hove M A and Somorjai G A 1986 *Surf. Sci.* **173** 351-65  
Saldin D K, Pendry J B, Van Hove M A and Somorjai G A 1985 *Phys. Rev. B* **31** 1216-8  
Starke U, de Andres P L, Saldin D K, Heinz K and Pendry J B 1988 *Phys. Rev. B* **38** 12 277-82.  
Steininger H, Lehwald S and Ibach H 1982 *Surf. Sci.* **123** 264-82