

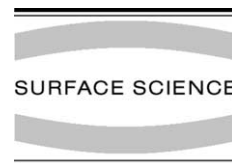


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Surface Science 543 (2003) 19–28



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# Structure determination of ordered and disordered organic molecules on a surface from the substrate diffraction spots in low energy electron diffraction: $(\sqrt{3} \times \sqrt{3})R30^\circ$ -C<sub>2</sub>H<sub>2</sub> and disordered CH<sub>3</sub>OH on Pd(1 1 1)

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Received 21 May 2003; accepted for publication 5 August 2003

## Abstract

We examine the effects of chemisorbed organic molecules on the intensity versus beam energy ( $I/E$ ) variation of the substrate  $(1 \times 1)$  Bragg spots in low energy electron diffraction (LEED). We find that these integer-order spots alone can provide important information about the local geometries of the molecules on the surface, largely independent of the degree of long-range order of an adsorbate overlayer. This is demonstrated by comparing LEED studies of two different adsorbates on Pd(1 1 1), namely: C<sub>2</sub>H<sub>2</sub> which forms an ordered  $(\sqrt{3} \times \sqrt{3})R30^\circ$  overlayer, and thus gives rise to superstructure (or fractional-order) Bragg spots, and disordered CH<sub>3</sub>OH, which scatters diffusely into directions between the integer-order spots. This allows LEED to be used conveniently for the determination of the structures of adsorbates on surfaces as a continuous function of coverage, independent of the degree of long-range order of the adlayer.

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**Keywords:** Chemisorption; Hydrides; Surface structure, morphology, roughness, and topography; Low energy electron diffraction (LEED); Palladium

## 1. Introduction

A knowledge of the changes of the structures of organic molecules on surfaces as a function of the coverage is a key ingredient to a fundamental understanding of processes of heterogeneous ca-

talysis. As the coverage is increased as a function of dose, adsorbates undergo a series of transitions between disordered and ordered phases, as monitored by low energy electron diffraction (LEED). A disordered phase is characterized by a LEED pattern that contains no additional Bragg spots over those formed by a clean surface (the so-called *integer-order* spots). Instead, the adsorbates scatter significant flux into the regions of the diffraction pattern between the Bragg spots, giving rise to what is known as a diffuse LEED pattern. In

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contrast, an ordered phase of a different periodicity to the substrate will generate extra Bragg spots (known as *fractional-order* spots). In either case, conventional wisdom suggests that information about ordered adsorbates may be found mostly from an analysis of the fractional-order spots, and that about disordered adsorbates from that of the diffuse intensities.

There have been a few studies of the intensity versus energy ( $I/E$ ) variation of the integer-order Bragg spots associated with the substrate's periodicity to determine the structures of disordered surfaces, for example that of Gauthier et al. [1] on the surface composition and structure of disordered alloys, and that of Schwennicke et al. [2] on the structure of the atomic adsorbates S/Ru(0001) and O/Ni(111). In the case of disordered *molecular* adsorbates on surfaces, such previous studies seem to have modeled the disordered surface by ordered unit cells of the same adsorbate coverage [3]. The latter calculations may involve large surface unit cells and may be very time-consuming. We show in this paper not only that the short-range information about the structure of *molecular* adsorbates and their local relation to the surface (which is of greatest significance to catalysis) may, in the cases of *both* ordered and disordered adsorbates, be most conveniently obtained by an analysis of the effects of the adlayer on the integer-order Bragg spots, but also that those intensities may be modeled by a LEED calculation for a  $(1 \times 1)$  overlayer with adsorbate scattering factors reduced by the magnitude of the coverage. Consequently, we suggest that it should be possible, by means of *rapid* LEED analysis, to follow the detailed changes in the structure of the adspecies as a *continuous* function of coverage *independent* of the degree of long-range order of the adlayer.

While it is true that surface structural probes such as surface extended X-ray absorption fine structure (SEXAFS), X-ray photoelectron diffraction (XPD), and even X-ray standing-wave methods may be used to study either ordered or disordered adlayers, all these techniques require access to synchrotron radiation sources, thus limiting their applicability. While scanning tunneling microscopy (STM) is capable of revealing real-space images of electron distribution of the out-

most surface layer, it is not well suited to determining the three-dimensional atomic structure of molecular adsorbates, and certainly not at the spatial resolution obtainable by diffraction methods. Through the analyses of the intensity *versus* beam energy ( $I/E$ ) variations of both integer- and fractional-order Bragg spots by means of computer-intensive analyses of large unit-cell structures, LEED has been used to determine the structures of a number of organic adsorbate systems [4,5]. Solution of structures of disordered adsorbates by LEED have been mostly attempted only through the experimentally challenging measurement of weak diffuse diffraction patterns [6–8]. Seitsonen et al. [3] analyzed the information in integer-order LEED  $I/E$  curves from disordered CO molecules located on half the symmetric bridge sites of a RuO<sub>2</sub>(110) substrate. In this case, the experimental data seem to have been modeled by an ordered, namely  $(2 \times 1)$  adsorbate structure with the same coverage as the disordered phase. The method proposed in the present paper involves a modeling of the adlayer by a small unit-cell (of the same size as the substrate unit cell) which is consequently much more rapid, and in the case of disordered surfaces, avoids the need to measure weak diffuse LEED intensities.

The last 15 years or so have seen the successful development of the fast perturbation scheme known as tensor LEED [9]. However, that method can be used only after the establishment of what is known as a reference structure, i.e. one that is known to be close to the actual structure, and for which a full multiple-scattering LEED calculation needs to be performed. The identification of such a reference structure is beyond the scope of any perturbation scheme, and must be performed by guesswork, or by means of a global search over parameter space. Our contention is that the data of the integer-order LEED spots from either a disordered or ordered unit cell of arbitrary size may be simulated by a LEED calculation for an adlayer of (small) unit cell size equivalent to that of the bulk, but with a reduced adsorbate scattering factor. A consequence is that, for small molecules, the number of parameters that need to be varied is sufficiently small to make a global structure search feasible with considerable saving in computational cost.

We will illustrate this idea by exploiting it to determine the structure of  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-C}_2\text{H}_2$  on Pd(1 1 1). Initially, a global structure search [10] will be performed using the data of only the integer-order LEED Bragg spots. We suggest that the best structure so found is then used as a starting point for structure refinement using a gradient search algorithm in an automated tensor LEED calculation [11]. We point out the similarity of this approach to that used earlier to determine the structure of disordered  $\text{CH}_3\text{OH}$  on Pd(1 1 1) [12]. For both systems, information contained in the integer-order Bragg spots proved to be sufficient to determine rapidly the important structural parameters of the adsorbates and their local bonding to the surface.

## 2. LEED theory of disordered surfaces

In LEED, the incident electron may be represented by a plane wave of wave vector  $\mathbf{k}_i$ . It may be expanded as a sum of incoming spherical waves of angular momentum quantum numbers  $L = (lm)$  about each atomic center

$$e^{i\mathbf{k}_i \cdot \mathbf{r}} / \sqrt{V} = \sum_L 4\pi i^\ell j_\ell(kr) Y_L^*(\hat{\mathbf{k}}_i) Y_L(\hat{\mathbf{r}}) / \sqrt{V}. \quad (1)$$

In the above expression,  $V$  is a volume normalization factor,  $j_\ell$  a spherical Bessel function,  $Y_L$  a spherical harmonic, and  $\mathbf{r}$  a position vector. The incoming waves are scattered by the adsorbates into a sum

$$\psi_{\text{sc}}(\mathbf{r}) = \sum_{jLL'} 4\pi i^\ell h_\ell^{(1)}(k|\mathbf{r} - \mathbf{r}_j|) Y_L(\mathbf{r} - \mathbf{r}_j) \times t_{LL'} Y_L^*(\hat{\mathbf{k}}_i) e^{i\mathbf{k}_i \cdot \mathbf{r}_j} / \sqrt{V} \quad (2)$$

of outgoing spherical waves, where  $h_\ell^{(1)}$  is a Hankel function of the first kind and  $t_{LL'}$  the scattering  $t$  matrix of each molecule.

Each scattered wave may be re-expanded as a sum of plane waves by using [13]

$$h_\ell(k|\mathbf{r} - \mathbf{r}_j|) Y_L(\mathbf{r} - \mathbf{r}_j) = \frac{i^{-\ell}}{2\pi k} \int \frac{d^2 \mathbf{k}_\parallel}{k_z} Y_L(\hat{\mathbf{k}}) e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_j)}. \quad (3)$$

Converting the integral into a sum using the appropriate density of states factor, and summing

over a number of adsorbates at positions  $\mathbf{r}_j$ , the scattered wave may be rewritten

$$\psi_{\text{sc}}(\mathbf{r}) = \sum_{\mathbf{k}_\parallel} M_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}} / \sqrt{V}. \quad (4)$$

In this equation,

$$M_{\mathbf{k}} = \sum_j \frac{2\pi i}{A k_z} e^{i(\mathbf{k}_i - \mathbf{k}) \cdot \mathbf{r}_j} f(\mathbf{k}, \mathbf{k}_i), \quad (5)$$

where  $f(\mathbf{k}, \mathbf{k}_i) = \frac{4\pi}{i k} \sum_{LL'} Y_L(\hat{\mathbf{k}}) t_{LL'} Y_L^*(\hat{\mathbf{k}}_i)$  is the scattering factor of the adsorbate molecule, and  $A$  a normalization area parallel to the surface. Here we have assumed the quasidynamical approximation in which multiple scattering within the adlayer is neglected [14].

Let  $\mathbf{k}_g = (\mathbf{k}_\parallel + \mathbf{g}, \mathbf{K}_{g_z})$  be the wave vector along the substrate beam direction, where  $\mathbf{k}_{g_z} = \sqrt{2E - (\mathbf{k}_\parallel + \mathbf{g})^2}$  is its component perpendicular to the surface,  $\mathbf{k}_\parallel$  the component of the incident wave vector parallel to the surface,  $E$  is the energy of the incident electrons, and  $\mathbf{g}$  a two-dimensional reciprocal lattice vector of the substrate. Then, since along the substrate Bragg directions, the electron waves interfere constructively, the interference sum

$$\sum_j e^{-i(\mathbf{k} - \mathbf{k}_i) \cdot \mathbf{r}_j} = \sum_{\mathbf{g}} m \delta_{\mathbf{k}_\parallel, \mathbf{k}_\parallel + \mathbf{g}}, \quad (6)$$

where  $m$  is the number of molecules. This equality is valid for every configuration of the statistical ensemble of the overlayer. It holds whether or not the molecules are ordered, provided they all occupy equivalent sites on the substrate lattice, as is usually the case for a chemisorbed overlayer. The observed intensity is a statistical average over all the configurations, each having the same interference sum. Substituting (6) into (5) we deduce

$$M_{\mathbf{k}} = \sum_{\mathbf{g}} \frac{2\pi i \Theta}{a k_{g_z}} f(\mathbf{k}_g, \mathbf{k}_i), \quad (7)$$

where  $\Theta$  is the coverage, and  $a$  the area of the substrate unit cell. Note that the wavefunctions representing the integer-order beams are proportional to  $\Theta$ , and independent of the degree of ordering of the adsorbate layer. Eq. (7) is equivalent to the average  $t$ -matrix approximation (ATA) commonly used in the studies of electron scattering

from disordered alloys [1,15] and atomic adsorbates [2].

Along directions away from the substrate Bragg spots, an ordered layer of molecules would give rise to extra overlayer Bragg spots (the fractional-order spots), while a disordered overlayer would scatter diffusely into all directions. For the latter case, it has been shown [12] that the measured signal in the diffuse part of the diffraction pattern would be expected to be much smaller than the contribution of the overlayer to the corresponding measurement of the Bragg spots for typical values of  $d\Omega$ , the solid angle subtended at the sample by the detector. When considering multiple scattering between disordered molecules and the substrate, effects of the diffuse intensities on the substrate spots may be ignored. As for an ordered molecular overlayer on a surface, the contribution of the fractional-order beams to the substrate Bragg spots' intensities involve at least two scatterings by the overlayer, which may be neglected to a first-order, an approximation also made in the *beam-set-neglect* method proposed by Van Hove et al. [16].

Within the quasidynamical approximation [14], the intensities of the integer-order Bragg spots from a surface containing an overlayer of coverage  $\Theta$  (whether ordered or disordered) are practically equivalent to those from a fictitious ordered layer of unit coverage of molecules of an effective scattering strength  $\Theta$  times that of the actual molecules [12]. The number of plane waves needed for the representation of the overlayer beam set [10] would be reduced by the same factor  $\Theta$  if the renormalized forward scattering (RFS) scheme [10,13] is used for the calculation of the interlayer scattering, or the number of atoms per unit cell of the substrate part of the composite layer will be smaller by a factor of  $\Theta$  in cases where the combined space method [10] is required for the calculation. This results in a reduction of the computational time by a factor of about  $\Theta^3$ , which even for a  $(\sqrt{3} \times \sqrt{3})$  overlayer is 1/27.

### 3. Experiment

LEED measurements were carried out in a doubly  $\mu$ -metal shielded ultrahigh vacuum cham-

ber operating at a base pressure of  $5 \times 10^{-11}$  Torr, and containing a Pd(111) single crystal, which could be cooled to 80 K and resistively heated to 1200 K. The sample was cleaned using standard procedures [17]. LEED patterns of the clean surface were photographed as a function of incident energy using a Nikon Coolpix digital camera (5.0 Mbytes resolution) and the images stored on an IBM Smartcard memory (1 GByte). The images were then downloaded to a personal computer for subsequent analysis. Diffraction patterns were collected initially from the clean surface for beam energies from 80 and 325 eV at 5 eV intervals, a procedure that took approximately 15 min. The sample was then heated briefly to 740 K to remove any background contaminants that may have adsorbed during this process, allowed to cool to 80 K and exposed to 1.5 L of acetylene to form a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure. Diffraction patterns of the adsorbate-covered surface were collected again at identical energies and again transferred to a microcomputer. The incident beam current was kept constant during the measurement of any particular set of  $I/V$  curves. The intensities of the spots for both the clean and adsorbate-covered surfaces were measured using NIH Image [18].

### 4. Clean surface of Pd(111)

The angles of incidence of the electron beam for both the clean and adsorbate-covered surfaces were determined using a standard LEED package [10] to find the best fit of calculated ( $I/E$ ) curves to the clean Pd(111) data. The contour map of the Pendry's  $R$ -factor [19] as a function of the incidence angles is shown in Fig. 1. From the location of the  $R$ -factor minimum, we determined that the polar angle of incidence is  $4^\circ$  to the surface normal and the azimuthal angle  $2^\circ$  from a plane normal to the surface passing through atoms in the first and second layer of substrate atoms.

### 5. Ordered overlayer: $(3 \times 3)R30^\circ$ -C<sub>2</sub>H<sub>2</sub> on Pd(111)

The molecular structure of acetylene (C<sub>2</sub>H<sub>2</sub>) on Pd(111) has been studied by spectroscopic tech-

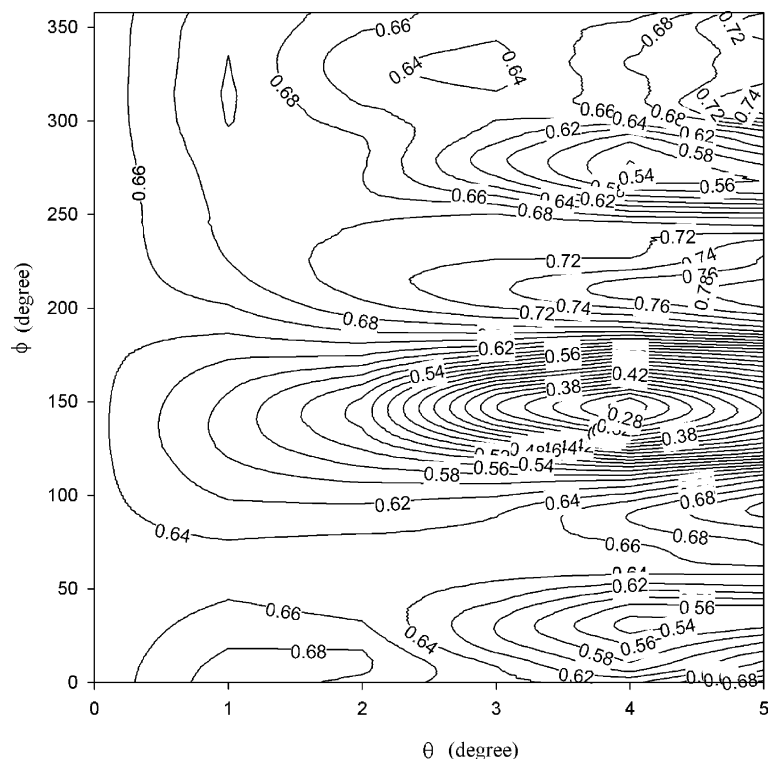


Fig. 1. Contour map of Pendry's  $R$ -factor as a function of polar angle ( $\theta$ ) and azimuthal angle ( $\phi$ ) of electron incidence for clean Pd(111).

niques such as high-resolution electron energy loss (HREELS) [20] and near-edge X-ray absorption fine structure (NEXAFS) [21]. More recently, scanned-energy mode XPD [22], STM and total energy calculations have also been used [23]. It was found that the C–C bond is substantially lengthened relative to its gas-phase value, indicating that interaction with the metal substrate leads to a weakening of the carbon–carbon triple bond.

For our global structure search, we only include integer-order beams and exclude the additional  $(\sqrt{3} \times \sqrt{3})R30^\circ$  beams. In order to restrict the number of parameters in this search, we assume that the C–C axis is parallel to the surface and fix the C–C bond length at 1.35 Å. These parameters will be relaxed in the final stage of our search. Therefore we are left with four parameters (H atoms are not included since they have a very small effect on the LEED intensities). The first two parameters are the  $x$  and  $y$  coordinates, within the

two-dimensional reduced first Wigner-Seitz cell, of one of the carbon atoms ( $C_1$ ), as shown in Fig. 2. Since the substrate has  $C_{3v}$  symmetry, the final intensity will consist of contributions from the six domains that can be generated by the operations of the  $C_{3v}$  rotational group on the molecule shown in Fig. 2. As the bond length is fixed, the second carbon atom ( $C_2$ ) can only rotate freely around a circle about  $C_1$ . The third parameter is the azimuthal angle  $\phi$  of  $C_2$  with respect to  $C_1$ . The last parameter is the height  $h$  of the C–C axis above the first layer Pd atoms. The global minimum was found to be located at  $h = 1.7$  Å. The contour map of the Pendry's  $R$ -factor as a function of the position of  $C_1$  for  $h = 1.7$  Å with the angular position of  $C_2$  ( $\phi$ ) optimized is shown in Fig. 3. The  $R$ -factor minimum is found at the bridge site of the substrate. (There is also a second minimum close to the first one with almost the same  $R$ -factor.) Next we place  $C_1$  at the bridge site and the

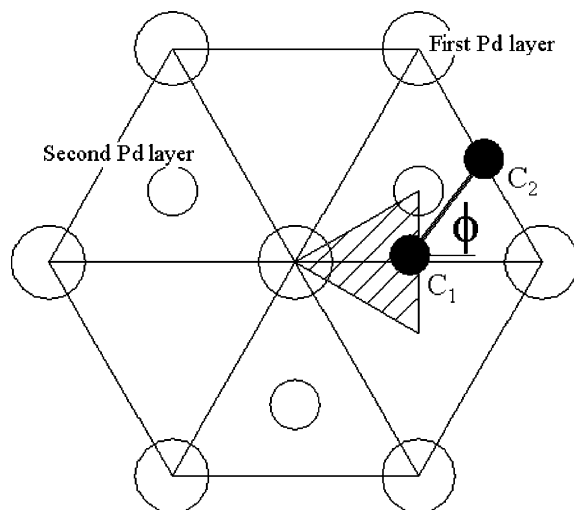


Fig. 2. Reduced first Wigner-Seitz cell in two dimensions (shaded area) of the clean Pd(111) surface. Also shown is the geometry relative to the substrate of the C atoms of a  $(\sqrt{3} \times \sqrt{3})R30^\circ$ -C<sub>2</sub>H<sub>2</sub> overlayer, as determined by the present work.

$R$ -factor as a function of the angular position of C<sub>2</sub> ( $\phi$ ) is shown in Fig. 4. A C–C bond located above an hcp hollow site is slightly favored over one above the fcc hollow site. All these are in qualitative agreement with previous structural results for C<sub>2</sub>H<sub>2</sub> on Pd(111) [20–23]. This establishes that the data in the integer-order Bragg spots alone can be used for a global search to determine the structure of an organic adsorbate.

Of course, in the case of an ordered overlayer, the extra information contained in the fractional-order spots may be used to *refine* this structure. Due to the fact that a LEED calculation for an overlayer of a larger unit cell is much more time consuming, a global structure search involving all the data is impractical. However, it is feasible to conduct a refinement of an initial (reference) structure from the above global search by including the extra experimental data and using a gradient search algorithm within an automated tensor LEED (ATL) [11] scheme. In practice, this would require the global search to be carried out on a much finer grid (which would still be much faster than a global search with the full beam set). In order to demonstrate the principle, we used the result of a total energy density functional theory

(DFT) calculation [23] a starting point for an ATL search. Since the ATL algorithm is based on the expansion up to the first order of amplitude about the reference structure, it contains some error unless the atomic displacements are very small. We moved the atoms to the minimum found by the algorithm and recalculated both the tensors and reference structure intensities. After 4 iterations, the atoms are found to move by less than 0.03 Å from the previous minimum values. Also we independently move the two carbon atoms parallel to the surface away from their optimal positions and show in Fig. 5 the  $R$ -factor as a function of the C–C bond length resulting from these movements. Since the  $R$ -factor depends on four variables and we are projecting the hypersurface onto a two-dimensional plane, the points do not lie on a single well-defined curve. The optimal Pendry's  $R$ -factor is 0.24. The final results compared with those from other works are shown in Table 1.

It is seen that the structure found agrees quite well with previous results except for the height of the C–C axis above the Pd substrate, which was found to be 1.7 Å in both the global and gradient searches. This could be due to the fact that the experimental conditions in the present study are slightly different from those of the other works. For example, in the XPD study [21], a structural analysis was done only on the  $(2 \times 2)$  phase of the system. Based on the similarities of the experimental data for the  $(\sqrt{3} \times \sqrt{3})$  and  $(2 \times 2)$  phases, it was concluded that the local geometry was similar, although no calculation was done for the former case. In the current study, the C–C axis was found to be almost parallel to the surface and that the molecule sits on top of the hcp hollow site.

Inclusion of the experimental data of fractional-order Bragg spots allows for a clear discrimination between adsorption probability on the fcc and hcp hollow sites. With the extra data, the  $R$ -factor for hcp hollow site adsorption was found to be considerably lower than that for fcc hollow site adsorption. This result is consistent with that of a total energy calculation [23], which gives an energy difference of 15 meV between the two sites. At 80 K, the Boltzmann factor is about 0.1, indicating that only about 10% of the fcc hollow sites would be expected to be occupied. A refinement of the

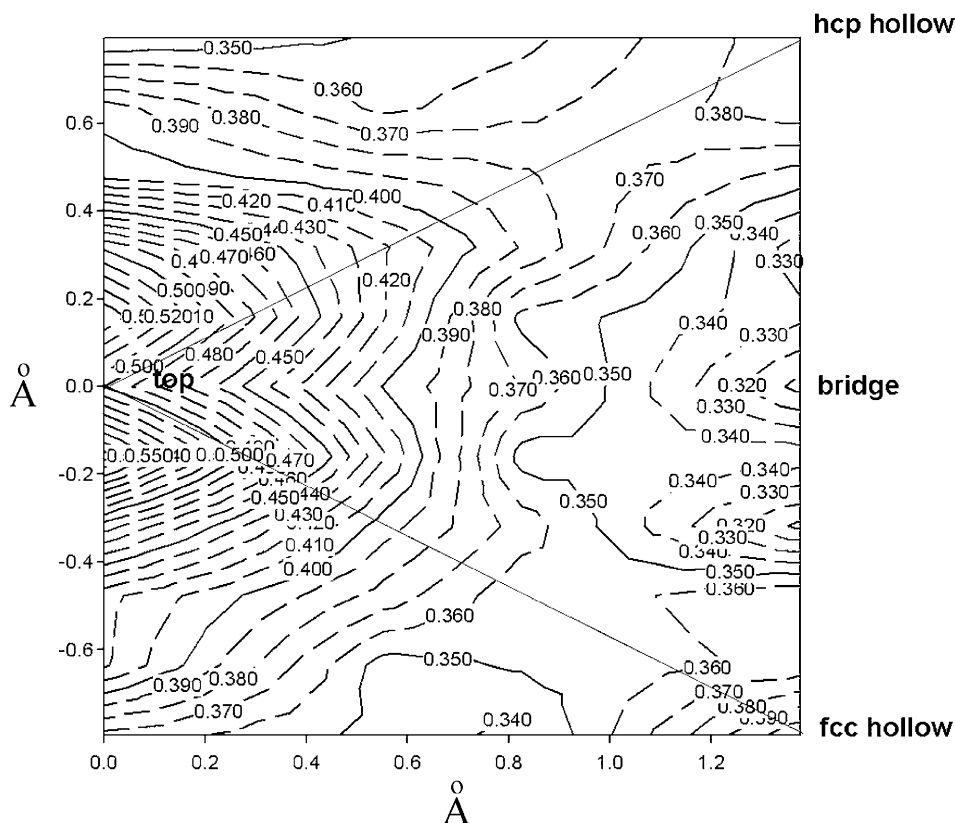


Fig. 3. Contour map of the Pendry's  $R$ -factor as a function of  $C_1$  over the reduced first Wigner-Seitz cell for  $(\sqrt{3} \times \sqrt{3})R30^\circ\text{-C}_2\text{H}_2$  on Pd(111), assuming a molecular height above the surface  $h = 1.7 \text{ \AA}$ .

structure with a gradient search based on the automated tensor LEED method [11] yields a C–C bond length of  $1.36 \text{ \AA}$ , which agrees quite well with the other results, and with the fact that the C–C bond is substantially lengthened and weakened compared with its gas-phase value. The optimized geometry of the C atoms relative to the surface is shown in Fig. 2.

## 6. Disordered overlayer: $\text{CH}_3\text{OH}$ on Pd(111)

We point out that exactly the same type of analysis of the data of integer-order Bragg spots may be used also to find the structure of disordered adsorbates, as shown by a recent determination of the structure of disordered methanol ( $\text{CH}_3\text{OH}$ ) on Pd(111) [12].

Most of the previous work on methanol ( $\text{CH}_3\text{OH}$ ) on metals had been concerned with the dissociated methoxy species,  $\text{CH}_3\text{O}$  which forms above  $120 \text{ K}$  [24–26]. It had been found that, in most cases, the adsorbed methoxy species stands upright relative to the surface on the fcc hollow sites. At  $80 \text{ K}$ , it had been shown that  $\text{CH}_3\text{OH}$  adsorbs molecularly on Pd(111) [27]. Molecular methanol does not form an ordered structure on Pd(111) and the lone pair electrons on the oxygen atoms interacting with the surface are expected to tilt the C–O axis away from the normal.

We recently performed an analysis [12], similar to that of the present paper, of the LEED intensities of the integer-order Bragg spots of an otherwise diffuse intensity distribution. In doing so, we exploited the fact that even a disordered layer of molecules on a subset of substrate lattice sites

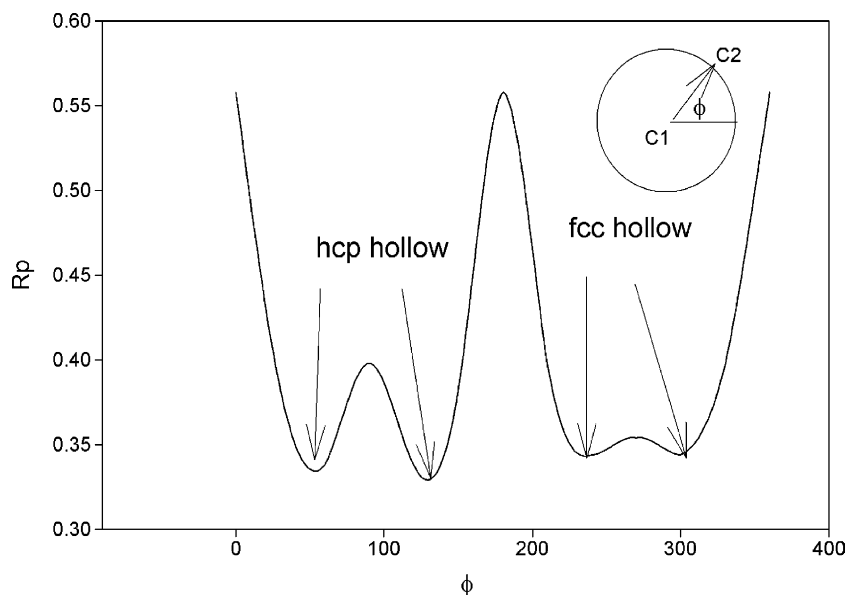


Fig. 4. Pendry's  $R$ -factor as a function of the angular position ( $\phi$ ) of  $C_2$  about  $C_1$ , which is fixed at the bridge site for  $(\sqrt{3} \times \sqrt{3})R30^\circ$ - $C_2H_2$  on Pd(111).

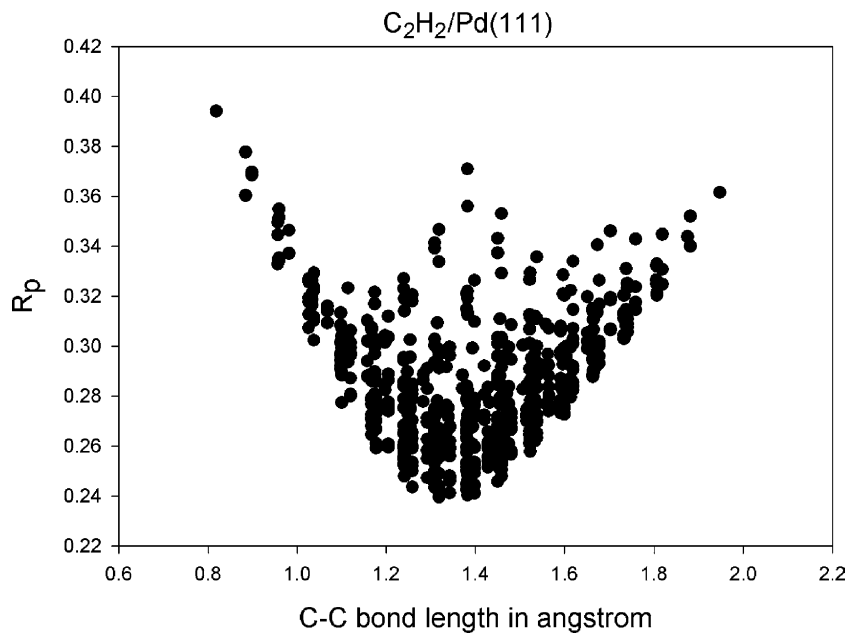


Fig. 5. Pendry's  $R$ -factor as a function of the C-C bond length for  $(\sqrt{3} \times \sqrt{3})R30^\circ$ - $C_2H_2$  on Pd(111).

scatter much more strongly into the directions of integer-order Bragg spots due to a *coherent* addition of adsorbate scattering into such directions

[12] than into those of the diffuse part of the diffraction pattern. Density functional calculations [12] confirmed the results of the LEED structural



Table 1

Comparison of structural parameters for  $(\sqrt{3} \times \sqrt{3})R30^\circ\text{-C}_2\text{H}_2$  on Pd(1 1 1) at 80 K from LEED measurements with results of vibration spectroscopy, XANES, PhD and total energy calculation

Reference	C–C bond length in Å	Tilt angle of C–C axis in degree	Distance of mid-point of C–C from the site center in Å	C–Pd distance in Å	Site	Temperature
Current work (LEED)	1.36	0.2	0.30	1.70	hcp hollow	80 K ( $\sqrt{3} \times \sqrt{3}$ )
Vibration spectroscopy [20]	1.42	0		1.55	hollow	>90 K ( $\sqrt{3} \times \sqrt{3}$ )
XANES [21]	1.30	0			hollow	100 K
PhD [22]	1.34	0	0.25	1.48	hcp hollow	160 K ( $2 \times 2$ )
Total energy [23]	1.36	0	0.22	1.57	hcp hollow	0 K

The site center is the centroid of the equilateral triangle formed by three nearest-neighbor Pd atoms.

Table 2

Comparison of the structural parameters for methanol on Pd(1 1 1) at 80 K from LEED measurements of the disordered overlayer with the results of density functional calculations

Parameter	LEED calculation	Density functional calculation
C–O distance (Å)	1.45	1.40
O–Pd distance (Å)	1.50	1.51
CO tilt angle (degrees)	15	15
Adsorption site	fcc three-fold hollow	fcc three-fold hollow

search, which found the C–O bond to be tilted about  $15^\circ$  from the normal. Details of the analysis can be found in that work, a summary of which follows.

As shown in Section 2, the intensity depends on both the coverage and local geometry of the molecule on the surface. The global search was conducted of the molecule at different adsorption sites that include the fcc and hcp hollows, the bridge and the atop positions. The C–O bond length was fixed at the gas-phase value of 1.427 Å. The polar and azimuthal angles of the C–O axis, the distance of the oxygen from the Pd substrate, the coverage and average thermal vibration amplitudes were all treated as variable parameters. It was found that the average vibration amplitude was about 0.13 Å and the coverage of methanol was about 0.3, which agreed well with that expected from the experimental methanol dose. The fcc hollow site was favored over all the others. The distance of O from the substrate was about 1.5 Å. However the *R*-factor was found to be insensitive to the azimuth of the tilted C–O axis. Fixing the molecule on the fcc hollow site, a structural analysis of the remaining parameters was conducted using the au-

tomated tensor LEED program [11]. The optimal Pendry's *R*-factor was found to be 0.23. The parameters of the structure determined finally is shown in Table 2.

## 7. Conclusions

It has been pointed out in this paper that integer-order LEED Bragg spots provide valuable information about the local geometries of both ordered and disordered adsorbate systems. The substrate spots' intensities are largely independent of the degree of ordering of the adsorbate layer. For the purposes of calculations, for both ordered and disordered overlayers, the adsorbate layer may be replaced by an ordered ( $1 \times 1$ ) layer with an effective scattering factor  $\theta$  times that of the actual molecules. This significantly reduces the computational cost for either ordered or disordered overlayers over calculations performed previously, and comparison with experimental data from just the integer-order spots allows the performance of a global search over the parameter space. This approach has been applied to both the ordered

adsorbate ( $\sqrt{3} \times \sqrt{3}$ )R30°-C<sub>2</sub>H<sub>2</sub> and the disordered adsorbate, CH<sub>3</sub>OH on Pd(1 1 1). We found that the results obtained from both systems agree well with previous results from different experimental techniques and also from total energy calculations.

For more complex disordered adsorbate systems, the number of unknown parameters may be too large for a complete structural search with the limited number of available integer-order data. In such cases, it may be necessary to enlarge the integer-order data sets by measuring the  $I/E$  intensities for different electron incident angles. In the case of an ordered overlayer, the information obtained from the global search with the integer-order data may serve as a reference structure for a subsequent refinement that includes the data of the fractional-order Bragg spots, as we have demonstrated for ( $\sqrt{3} \times \sqrt{3}$ )R30°-C<sub>2</sub>H<sub>2</sub>/Pd(1 1 1). For a disordered overlayer, in principle, a similar refinement could be performed by including the weak diffuse intensities, assuming they could be measured reliably.

Since this method of analyzing integer-order Bragg data applies equally well to ordered and disordered adsorbates, and does not rely on measurement of weak diffuse background signals, it opens up the possibility of conveniently determining the structures of a wide range of adsorbate systems.

### Acknowledgements

WTT was supported by DOE grant DE-FG02-92ER14289 and DKS by DOE grant DE-FG02-84ER45076 and NSF grant DMR-9815092.

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