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SYMMETRY EXTINCTION OF LEED BEAMS FOR NAPHTHALENE ADSORBED ON P--ETC(U)
SEP 81 D DAHLGREN, J C HEMMINGER

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Symmetry Extinction of LEED Beams for
Naphthalene Adsorbed on Pt(111)

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Abstract

The LEED pattern obtained for Naphthalene on Pt(111) is well described by an ordering which consists of three equivalent domains of a (6x3) overlayer. The existence of a glide symmetry in the overlayer is confirmed by the angular dependence of the symmetry extinction of several LEED beams.

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Considerable effort has been expended during the past few years to carry out detailed analysis of the intensity versus voltage data obtained in LEED studies of ordered overlayers of small hydrocarbons on metals.^(1,2) The complexity of the structural problem coupled with the multiple scattering nature of LEED has made the determination of unique structures for systems even as seemingly simple as acetylene and ethylene on Pt(111) a difficult endeavor.⁽³⁻⁵⁾ It is generally recognized that symmetric unit cells for an overlayer can lead to the extinction of some of the diffracted beams for all incident electron energies.⁽⁶⁻⁸⁾ Such symmetry extinctions can be seen quite easily from simple kinematical calculations of the unit cell structure factor, $(F(h,k))$. These extinctions can be shown to carry over into the complete multiple scattering formalism for cases in which the substrate also has the particular symmetry element.^(7,8) Thus when such energy independent extinctions occur they can provide an enormous advantage in the complete analysis by severely restricting the possible internal structure of the overlayer unit cell. This appears to be the case for naphthalene adsorbed on Pt(111). In initiating a study of the chemistry of naphthalene and azulene on Pt(111) we have reinvestigated the LEED pattern for naphthalene on this face of Pt. Gland and Somorjai observed LEED patterns and carried out work function measurements for this system and proposed a model for the structure of the naphthalene overlayer.⁽⁹⁾ They labelled the diffraction pattern as a (6×6) . Subsequently, Firment recognized that not all the

beams expected of a (6x6) could be seen.⁶ Firment proposed a structure for the overlayer, possessing two glide symmetries, which would cause the extinction of the "missing" beams.⁶ We have utilized the dependence of the symmetry extinction on the angle of incidence of the electron beam to confirm the existence of the glide symmetry.

Upon adsorption at room temperature the naphthalene LEED exhibits a partially segmented, diffuse, 1/3 order ring, (Figure 1) indicative of a molecular spacing three times the Pt-Pt spacing but with domains which have a random rotational orientation with respect to the Pt substrate. The Auger spectrum of such an overlayer shows a carbon to platinum atom ratio of 1.1.⁽¹⁰⁾ This carbon to platinum ratio is consistent with the packing of molecules every 3 Pt atoms. If the sample is then gently annealed in vacuum at 100°C the LEED pattern shown in Figure 2a is obtained. The dominant features of this pattern are those of a simple (3x3) structure.. There are additional weak beams which make the pattern "similar" to a (6x6). The model which we propose for the naphthalene overlayer structure is shown in Figure 3. This is based on three equivalent domains of a (6x3) unit cell. In the absence of any symmetry within the unit cell the three equivalent domains of a (6x3) unit cell will give rise to a diffraction pattern the same as a (6x6) unit cell.¹¹

The observed LEED pattern in Figure 2 fits this unit cell with the exception of several conspicuously missing beams. In particular the (n,n) beams, with n an odd integer and the (k,0)

beams with k an odd integer are not observed at any incident electron energy, when the electron beam is incident perpendicular to the surface.¹² The extinction of the (n,n) beams is predicted by the glide symmetry parallel to the b axis in figure 3. The extinction of the $(k,0)$ beams is due to the glide symmetry perpendicular to the b axis.

The fact that the non-existence of these beams is indeed due to a glide symmetry may be established by observing the LEED pattern for an incident electron beam which is not perpendicular to the surface. The glide symmetry involves a translation followed by a reflection through the glide plane. For this to be a symmetry of the experiment the incident electron beam must be perpendicular to the surface, or must lie in the glide plane. Thus, by rotating the sample such that the electron beam is no longer incident perpendicular to the surface, we should see intensity appearing in the previously non-existent beams. In addition we should be able to distinguish between the three domains by having the incident electron beam remain in the glide plane for one of the domains while we rotate away from perpendicular incidence. This will result in intensity in the "missing" beams for two of the domains while the beams from the third domain are still extinguished. The result of one such experiment is shown in figure 4. In this experiment the electron beam is incident on the surface ~ 10 degrees away from the surface normal. However the incident electron beam is in the glide plane perpendicular to the b axis of one

of the three domains. It can be seen in figure 4 that the (7,0), and (5,0) beams for two of the domains have non-zero intensity while the (7,0) beam of the third domain still shows no intensity. The diffraction beams corresponding to large reciprocal lattice vectors are most sensitive to the symmetry breaking described above. This is easily understood since the symmetry extinction is caused by interference of beams scattered from identical scattering centers connected by the glide symmetry. The beams corresponding to large reciprocal lattice vectors have high frequency phases. The high frequency phase results in more stringent requirements for the complete destructive interference of beams from several scattering centers. This is why we see (figure 4) intensity in the (7,0) and (5,0) beams and not the (3,0) or (1,0) beams when the symmetry is broken.

The (6x3) model of figure 3 is also consistent with the distinctive intensity pattern seen for the remaining beams. The brightest beams are the 1/3 and 2/3 order beams, while the additional 1/6, 3/6, 5/6 order beams are quite weak. This is consistent with the model since all three equivalent domains of the (6x3) structure contribute to the 1/3 and 2/3 order beams, while each of the 1/6, 3/6, 5/6 order beams have intensity contributions from only 1 or 2 domains.

We should point out that the glide symmetry parallel to the b axis is a symmetry of only the overlayer and the first Pt layer. This leads to a possibility of predicted intensity in the (n,n) beams from multiple scattering involving the na-

phthalene overlayer with the second or third Pt layers. However, these beams are expected to be weak in any case since they have intensity contributions from only one domain and we are not surprised that multiple scattering from lower Pt layers does not make them observable.

The structure we propose for naphthalene on Pt(111) is consistent with the following experimental observations:

1. The carbon/platinum atom ratio.
2. The energy independent, angular dependent, extinction of the $h=k=\text{odd integer}$, and $h=\text{odd integer}$, $k=0$ beams.
3. The qualitative relative intensities of the observed beams.

Beyond the existence of the glide symmetries we can not, from this simple analysis, determine the specific orientation or registry of the naphthalenes with respect to the Pt substrate. However, the glide symmetries do severely restrict the possible overlayer structures. While we can not rigorously exclude structures in which the naphthalene plane is not parallel to the surface, the combination of molecular spacing (every 3 Pt atoms) and glide symmetries fit very well with the naphthalene molecular size, for a structure which has the molecular plane parallel to the surface. It is important to note however that any proposed structure with the naphthalene plane not parallel to the surface must retain the glide symmetry.

We would suggest that the naphthalene/Pt(111) system would be an exceptionally good candidate for a complete LEED intensity

analysis. As described above the structural parameters are severely restricted due to the distinctive relative intensities of the beams.

We would like to thank M.A. Van Hove, and L. Firment for several useful discussions. This work was supported in part by the Office of Naval Research and the Hooker Chemical Corporation Grant of Research Corporation. Support by the Focused Research Program in the Chemistry and Physics of Crystal Surfaces at UCI is also acknowledged.

Figure Captions

Figure 1. LEED pattern obtained after adsorption of naphthalene on Pt(111) at room temperature. The specular beam appears just below the shadow of the crystal holder.

Figure 2a. LEED pattern of naphthalene on Pt(111) after annealing at 100°C.

Figure 2b. Drawing of LEED pattern shown in Figure 2a. The beams missing from three domains of a (6 x 3) pattern are indicated by open circles. The Pt first order beams are indicated by an x.

Figure 3. Model of the ordering of naphthalene on Pt(111). Only one of the three equivalent domains is shown (the hydrogens have been omitted for clarity). The glide symmetries are indicated as dashed lines.

Figure 4a. LEED pattern with incident electron beam not perpendicular to the surface. The incident beam lies in the glide plane perpendicular to the b axis of one of the three domains.

Figure 4b. Drawing of the LEED pattern of Figure 2a. The (7,0) and (5,0) beams which now show intensity are indicated by Δ . The (7,0) beam with zero intensity is indicated by O. The Pt first order beams are indicated by an x.

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12. We are using an indexing system based on the overlayer unit cell.

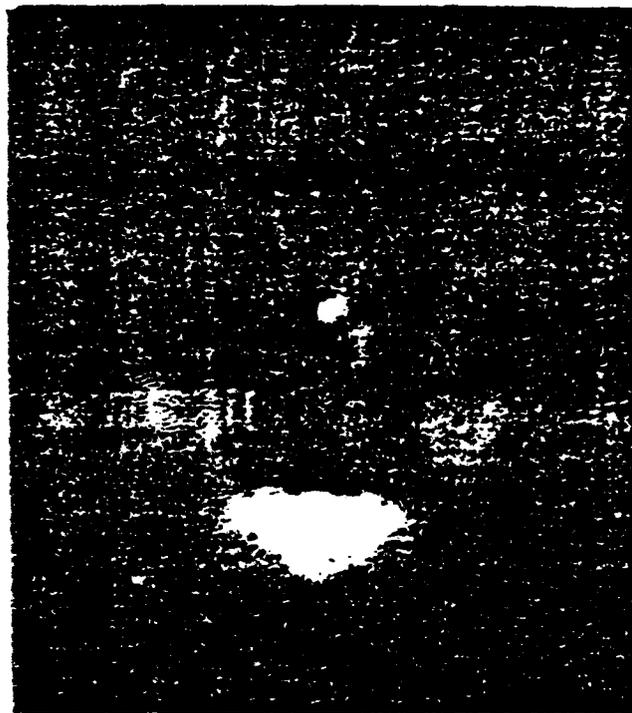
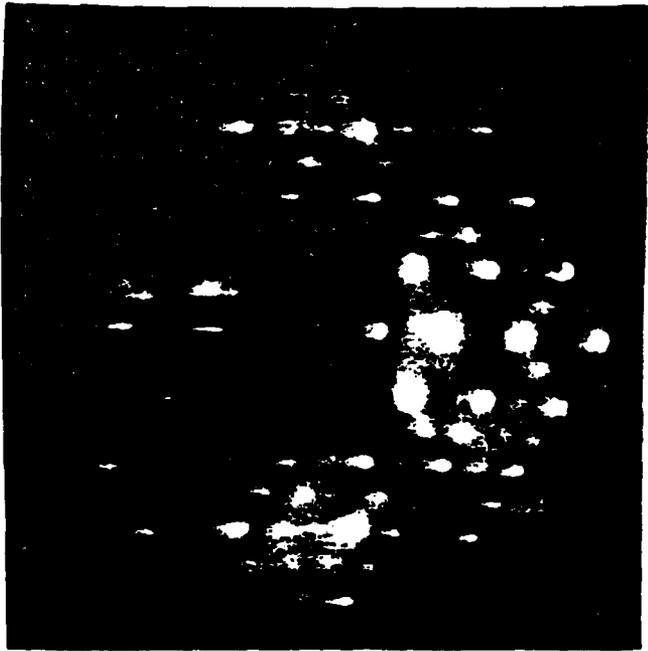
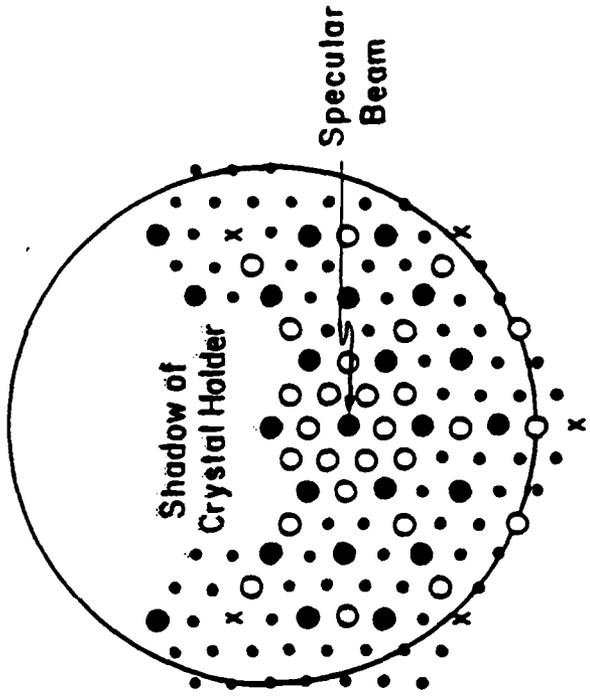


Fig 1



a



b

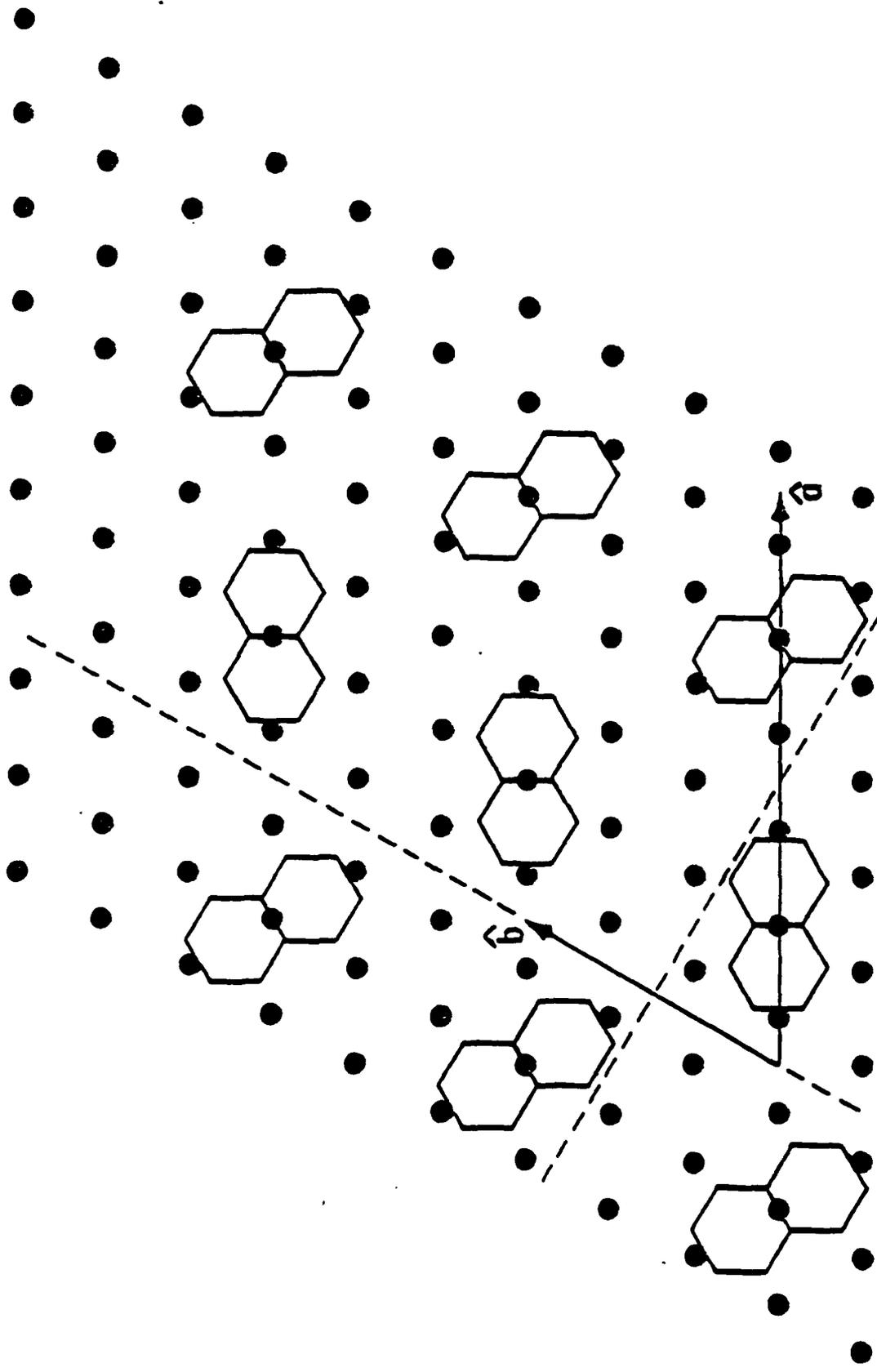
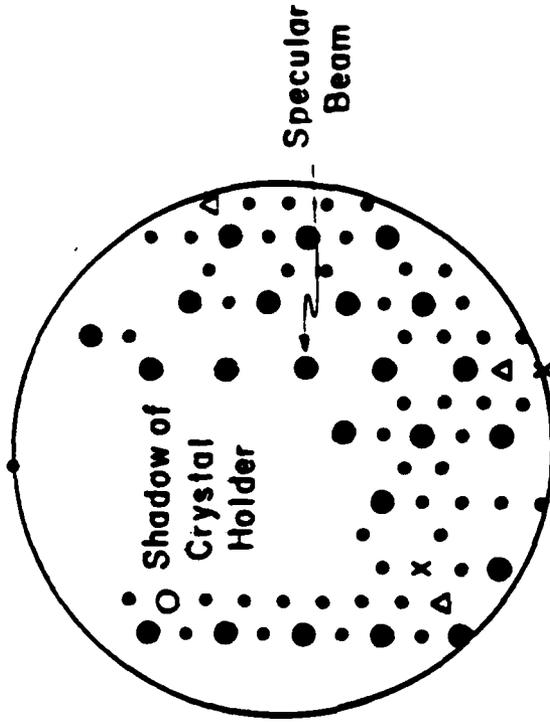


Fig 3



a



b

Fig 4

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