

LEED and HREELS studies of benzene adsorbed on Rh(111)

M A Van Hove, Rongfu Lin, R J Koestner, B E Koel, M Mate, J E Crowell and G A Somorjai, *Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, USA*

We have studied the adsorption behaviour of benzene (C_6H_6) deposited on the Rh(111) single-crystal surface in the temperature range of 220 to 800 K. The techniques used were low-energy electron diffraction (LEED) and high-resolution electron energy loss spectroscopy (HREELS), in addition to thermal desorption spectroscopy (TDS) and Auger electron spectroscopy (AES).

The Rh(111) surface was prepared by conventional methods, as reported previously¹ and the benzene was adsorbed to saturation from the gas phase, usually at 240–300 K. The experiments were performed in two separate vacuum chambers. TDS measurements indicate that only small amounts of C_6H_6 desorb from the benzene-covered surface until about 390 K. A major H_2 TDS peak is observed at about 413 K, which is interpreted as due to benzene decomposition. The molecules dehydrogenate further to lose H_2 to the gas phase in a broad desorption state from 420 to 670 K. Specular and off-specular HREELS measurements give simple spectra consistent with intact benzene molecules that lie flat on the surface up to the decomposition temperature, under all explored conditions. These spectra are very similar to those obtained by Bertolini *et al*² and by Lehwald *et al*³ on Pt(111) and Ni(111), and are therefore not reproduced here. Using HREELS, we infer that the molecules decompose mainly into CH_n fragments, with some evidence also for remaining C—C bonds.

Four different sharp LEED patterns were observed. Most reproducible were a $\begin{pmatrix} 3 \\ 1 \\ 3 \end{pmatrix} = c(2\sqrt{3} \times 4)\text{rect}$ pattern and a $\begin{pmatrix} 3 \\ 0 \\ 3 \end{pmatrix} = (3 \times 3)$ pattern (the 'rect' notation indicates a centred rectangular unit cell with sides $2\sqrt{3}$ and 4 times the substrate surface lattice constant). The other observed patterns were $\begin{pmatrix} 3 \\ 2 \\ 3 \end{pmatrix} = (2\sqrt{3} \times 3)\text{rect}$ and $(\sqrt{7} \times \sqrt{7})R19.1^\circ$. The sizes of the four corresponding unit cells are 8, 9, 12 and 7, respectively, in terms of the number of surface Rh atoms included. The unit cells of size 7, 8 and 9 are compatible with known Van der Waals dimensions of flat-lying benzene molecules, assuming one molecule per cell; the $(2\sqrt{3} \times 3)\text{rect}$ unit cell could contain either two very crowded flat-lying molecules or one flat-lying molecule with much room to spare.

The $\begin{pmatrix} 3 \\ 1 \\ 3 \end{pmatrix}$ and (3×3) structures have a well-characterized temperature behaviour. The $\begin{pmatrix} 3 \\ 1 \\ 3 \end{pmatrix}$ structure exists up to about 370 K, where it transforms irreversibly to the (3×3) structure. The (3×3) structure is very stable up to about 395 K, where it disorders (just prior to the first H_2 desorption peak in TDS). There are indications that the (3×3) structure might be stabilized by carbonaceous fragments resulting from partial benzene decomposition or from impurities that have diffused to the surface at the higher temperatures.

Both the existence of commensurate overlayer structures and the high desorption temperature of benzene on Rh(111) (one state at about 410 K) indicate strong metal-carbon bonds, which in the flat-lying geometry would involve the π -orbitals of the benzene ring. Strong bonding to the metal could distort the molecules: e.g. C—C bond length expansions and C—H bond bending away from the surface can be expected, in analogy with acetylene and ethylene adsorption on metals⁴ and with benzene structures in organometallic clusters⁵. However, HREELS shows that the

surface complex probably retains a high symmetry of type $C_{3v}(\sigma_d)^6$, at least for the $\begin{pmatrix} 3 \\ 1 \\ 3 \end{pmatrix}$ state.

By comparing measured and calculated LEED I-V curves, we have analyzed the detailed position of the adsorbed benzene molecules in the $\begin{pmatrix} 3 \\ 1 \\ 3 \end{pmatrix}$ and (3×3) structures. The I-V curve measurements used the photographic technique, coupled with microdensitometry and a computer program to obtain spot intensities⁷. The theoretical calculations were based on the combined-space method⁸, using Reverse Scattering Perturbation (RSP)⁹ within the overlayer and Renormalized Forward Scattering¹⁰ between all layers. Hydrogen could be completely ignored in all cases.

Three levels of approximation were applied in calculating the overlayer diffraction matrices¹⁰. In a first set of calculations, all multiple scattering within the overlayer was neglected (yielding kinematic layer diffraction matrices). This has been shown to allow an economical scan through many structural models that are a priori plausible². A more detailed structural search among the more promising structures was performed by including multiple scattering between all pairs of bonded carbon atoms ('near-neighbour multiple scattering only'). A final refinement or confirmation of the best structure can be carried out with all multiple scattering included, as in conventional RSP.

We also tested another economically attractive computational scheme, which we call 'unit-cell reduction method'^{13,14}. It is best explained for the (3×3) structure. The (3×3) pattern contains certain spots that would also be present for a (3×1) structure, e.g. the $(n/3, 0)$ spots. Therefore, one could make a calculation for a (3×1) structure of the same short-range order as the (3×3) structure (i.e. same adsorption site, etc) and expect to find some similarity in the intensities of common spots; the similarity would be perfect in the kinematic limit. In the present case of benzene, dissimilarities would result mainly from multiple scattering between different molecules, which is weak. Our calculations support the conclusion that the unit-cell reduction method gives reliable results. In the (3×3) case, three rotated domains of (3×1) structure and one domain of $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure reproduce all (3×3) beams; both reduced unit cells have an area smaller by a factor 3 from the (3×3) unit cell and yield correspondingly smaller computational costs.

For both the $\begin{pmatrix} 3 \\ 1 \\ 3 \end{pmatrix}$ and (3×3) structures, we have so far investigated about 500 structural models, differing in the following respects:

- metal-molecule interlayer spacing (ranging from 1.2 to 4.2 Å);
- adsorption site (molecular centre positioned over top site, two different hollow sites and bridge site);
- azimuthal orientation of the molecules about their six-fold axis (including freely spinning molecules);
- buckling (towards chair-shape or boat-shape of cyclohexane);
- planar distortions (uniform expansion or differential C—C bond length expansion).

Theory and experiment were compared with five different R-factor formulae and their average. In the $\begin{pmatrix} 3 \\ 1 \\ 3 \end{pmatrix}$ case, preliminary results strongly favour a hollow adsorption site (over a Rh atom in the second metal layer); each of the three metal atoms around the hollow site would be bonded to two carbon atoms equidistant at about 2.35 ± 0.1 Å (this corresponds to a planar molecule with a metal-molecule layer spacing of 2.15 ± 0.1 Å), slightly larger than corresponding values in organometallic clusters containing aromatic rings, which show Rh—C bond lengths of 2.09 to 2.40 Å¹⁵. In the (3×3) case, no structural model has so far given satisfactory agreement between theory and experiment.

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Hydrogen-induced W(100) surface reconstruction: lattice dynamical effects

E F J Didham and R F Willis, *Cavendish Laboratory, Dept Physics, University of Cambridge, CB3 0HE, UK*

Hydrogen coverage dependent studies of the W(100) surface indicate that the surface reconstructs from a (1×1) ordered lattice to a $(\sqrt{2} \times \sqrt{2})$ commensurate structure at very low coverages (≤ 0.05 saturation coverage)¹. High resolution electron energy loss studies show that this involves the pinching together of pairs of substrate W atoms with the hydrogen occupying a bridge site between W pairs². Temperature dependent results suggest that a first order phase transition occurs from the commensurate $(\sqrt{2} \times \sqrt{2})$ to the (1×1) ordered phase, i.e. depopulation of a 'pinched-dimer' into a 'relaxed-dimer' state³.

With increasing coverage (≈ 0.15 saturation coverage), the experimental results reveal a commensurate-incommensurate phase transition which occurs via a tilted dimer model for the incommensurate phase⁴. The combination of both lateral and vertical displacements of the W atoms is indicative of a mixing between two lattice vibrational modes: a Rayleigh phonon branch with displacements normal to the surface, and a phonon branch with displacements in the surface⁵. This coverage dependent transition suggests that the incommensurate phase occurs via a lattice dynamical 'tilt-waves' mechanism in which the W dimers are rotated about the surface plane. The vibrational frequencies are intermediate between the two states ('pinched' and 'relaxed') with the hydrogen preferentially occupying the pinched dimer state.

The hydrogen-induced phase transitions on the W(100) surface can perhaps be best visualized in terms of the formation of periodic lattice distortion waves, which propagate over the surface wavelength and amplitude, depending on the experimental

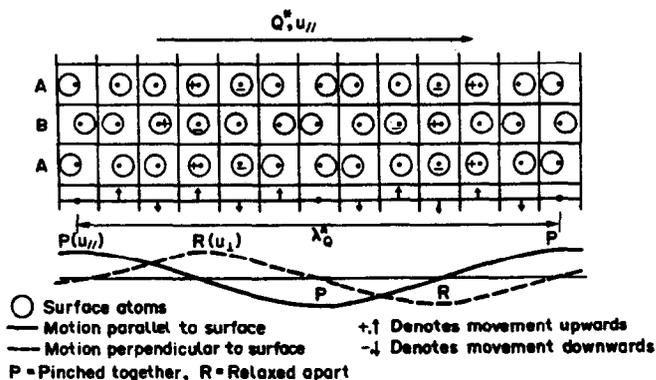


Figure 1. Structural model of the incommensurate periodic lattice distortion waves produced by hydrogen chemisorption on W(100). The H atoms occupy the pinched surface-lattice sites (p, u_1) at low coverages. The displacements of the surface tungsten atoms are shown relative to the undistorted bulk lattice (dots within square mesh), with up and down displacements indicated by \pm signs. The coupled phonon modes are shown by the out-of-phase sinusoidal curves below.

conditions. Our model, which is an extension of the ideas of Tosatti *et al*⁶ and Heine and McConnell⁷ is shown in Figure 1. The surface atoms are displaced by a mixture of horizontal and vertical displacements due to coupled phonon modes; the simplest sinusoidal wave is illustrated in Figure 1. The wavelength of the incommensurate wave λ_{Q^*} of wavevector Q^* identifies the periodicity. Higher Fourier components produce a square waveform which closely approaches a model of static domains of pinched together atoms separated by regions of high phase slip due to predominantly up-and-down atomic displacements. The up-and-down displacements only preserve mirror symmetry in the surface if Q^* is parallel to the pinched displacements. Also, computer simulated LEED studies⁸ show that it is important to include several layer atomic displacements in order to accommodate the top layer shifts indicated in Figure 1. With increasing hydrogen coverage (> 0.25 saturation), one dimensional disorder occurs across the linear periodic lattice distortion 'chains' A, B, A etc, producing streaking of the satellite spots^{1,9}.

The reflection electron energy loss results are sensitive to the local point group symmetry of the H modes which change in a subtle way with these periodic lattice distortions⁴. Our model suggests that the H atoms are quantum mechanical particles which diffuse quite readily across the surface producing polaron-type trapping at the pinched lattice sites¹⁰.

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