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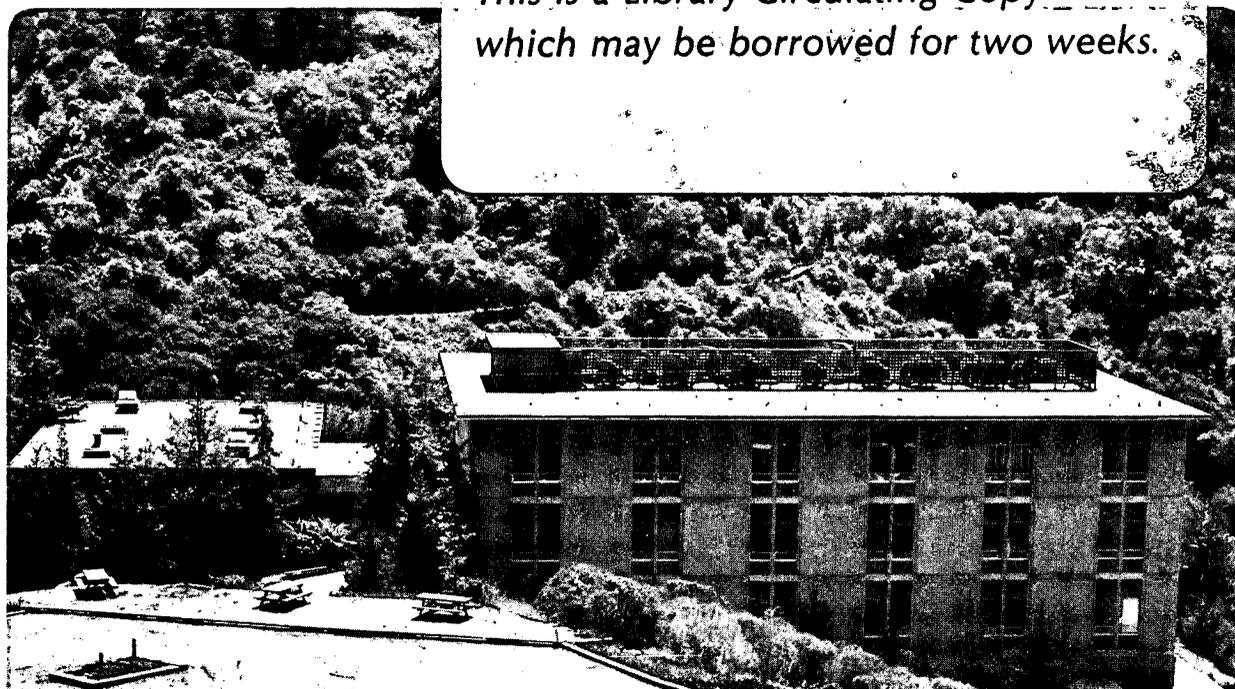
### The Structure of Benzene Adsorbed on Pd(111): A Dynamical LEED Study

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## The Structure of Benzene Adsorbed on Pd(111): A Dynamical LEED Study

H. Ohtani, M.A. Van Hove and G. A. Somorjai

Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory  
and Department of Chemistry, University of California, Berkeley, CA 94720

The structure of benzene adsorbed on Pd(111) has been studied by a dynamical LEED (Low-Energy Electron Diffraction) analysis as a step in understanding the capability of this surface to form benzene by trimerization of acetylene molecules.

Any pure benzene overlayer on the Pd(111) surface is disordered at room temperature. However coadsorption of benzene and CO on Pd(111) yields a new surface periodicity with (3x3) unit cell (relative to the (1x1) substrate periodicity). HREELS (High-Resolution Electron Energy Loss Spectroscopy) and TDS (Thermal Desorption Spectroscopy)<sup>1</sup> imply that one benzene molecule and two CO molecules are adsorbed associatively over hollow sites in each (3x3) unit cell<sup>1</sup>. This coadsorbed structure, Pd(111)-(3x3)-C<sub>6</sub>H<sub>6</sub>+2CO, was analyzed with dynamical calculations of LEED intensities to yield detailed bond lengths information<sup>2</sup>. In total, approximately 1500 distinct structures were examined. Several approximation methods were applied to analyze this complicated coadsorption structures: beam set neglect, near-neighbor multiple scattering, and kinematic sublayer addition<sup>3</sup>. The structural result is shown in Figure 1. In this structure, both benzene and CO are adsorbed over fcc-type hollow sites in a close-packed lattice. *The benzene ring skeleton is found to be nearly indistinguishable from the gas phase structure on Pd(111) surface.*

In Table 1, the molecular structure of benzene on Pd(111)<sup>2</sup> obtained is compared with previously studied benzene structures on Rh(111)<sup>4,5</sup> and Pt(111)<sup>6</sup>. In all cases, benzene is coadsorbed with CO to produce well-ordered superlattice. As shown in this table, the carbon rings tend to expand upon chemisorption. The

metal-carbon bond lengths ( $d_{M-C}$ ) decrease and the benzene ring expands from Pd(111) to Rh(111) to Pt(111), indicating increasing benzene-metal interaction in that order. This order of interaction is supported by the HREELS data, where the frequency of the  $\gamma_{CH}$  (out of plane CH bending) mode increases from Pd(111) to Rh(111) to Pt(111)<sup>1,7-10</sup>. On Rh(111) and Pt(111), where strong benzene-metal interactions have been detected by LEED as evidenced by shorter metal-carbon bond lengths, the benzene rings show relatively long and short C-C bonds within the molecule. In these cases the benzene molecules adopt the same symmetry as their adsorption sites: benzene adsorbed at bridge sites of Pt(111) shows an in-plane distortion with  $C_{2v}$  symmetry, and benzene adsorbed at hollow sites of Rh(111) shows a Kekulé distortion with  $C_{3v}$  symmetry. It is therefore probable that weak Kekulé type distortion does exist in the case of Pd(111), but is too small to be confirmed by LEED. Any out-of-plane distortions of the  $C_6$  ring have not been detected on these three surfaces.

Benzene decomposes on Rh(111) through an acetylene-like intermediate<sup>11</sup>. On supported Rh particles, benzene to acetylene conversion occurs with coadsorbed CO<sup>12</sup>. These may be related to the strong metal-benzene interactions and the Kekulé type distortion of benzene molecules observed on Rh(111) surface. Pd(111) surface, on the other hand, catalyze acetylene to benzene conversion<sup>13-18</sup>. The weak benzene-palladium interaction may be related to the capability of Pd(111) surface to catalyze this reaction, since weakly bonded benzene, as detected by LEED, should easily desorb molecularly after this conversion proceeds on this surface.

### Acknowledgements

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under contract No. DE-AC03-76SF00098. We also acknowledge super-computer time provided by the Office of Energy Research of the U.S. Department of Energy. H. Ohtani gratefully acknowledges financial support from IBM Japan.

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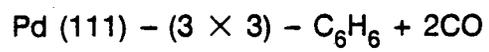
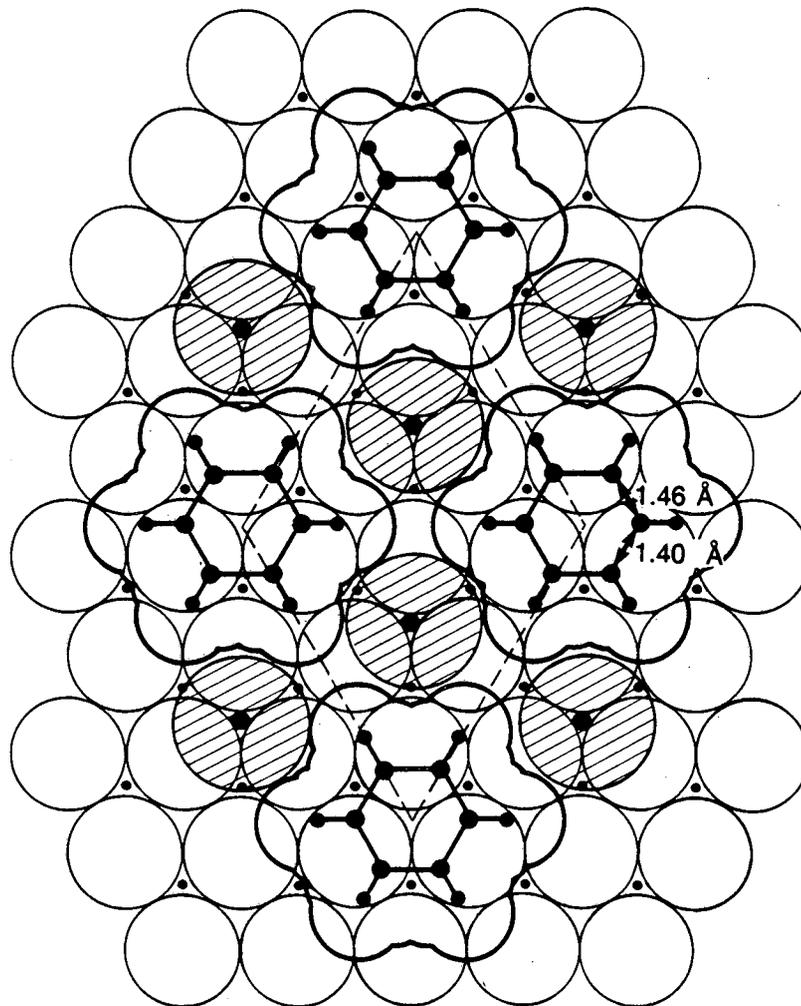
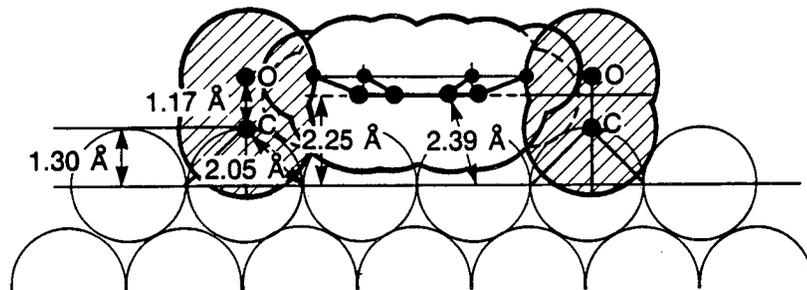
### Figure caption

**Figure 1.** Optimal structure for Pd(111)-(3x3)-C<sub>6</sub>H<sub>6</sub>+2CO, determined with LEED. Van der Waals shapes are used for overlayer molecules. The CO molecules are shown shaded. The hydrogen positions are guessed.

### Table caption

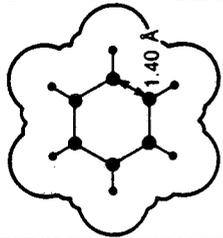
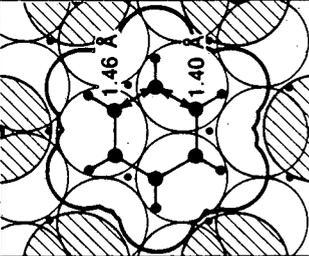
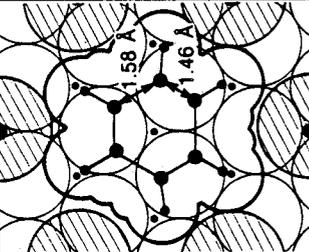
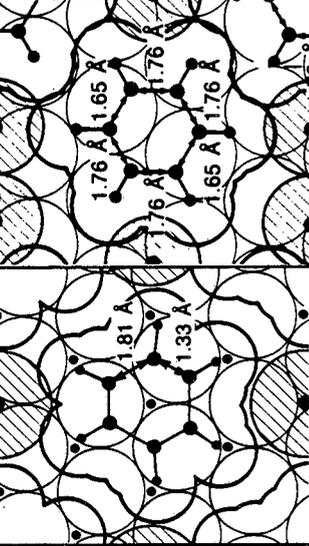
**Table 1.** Structures of benzene on Pd(111), Rh(111), and Pt(111)

\*) The out of plane CH bending frequency of benzene. For each surface, the frequency range indicated includes the values of the pure benzene overlayers and coadsorbed superlattices with CO.



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Fig. 1

Substrate	(Gas Phase)	Pd(111)	Rh(111)	Pt(111)
Surface Structure		(3x3)-C <sub>6</sub> H <sub>6</sub> + 2CO	(3x3)-C <sub>6</sub> H <sub>6</sub> + 2CO + CO	(2√3x4)rect-2C <sub>6</sub> H <sub>6</sub> +4CO
The Structure of Benzene				
C <sub>6</sub> Ring Radius (Å)	1.40	1.43±0.10	1.51±0.15	1.72±0.15
d <sub>M-C</sub> (Å)	-	2.39±0.05	2.30±0.05	2.25±0.05
γ <sub>CH</sub> (cm <sup>-1</sup> ) <sup>*</sup>	670	720-770	780-810	830-850

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Table 1

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