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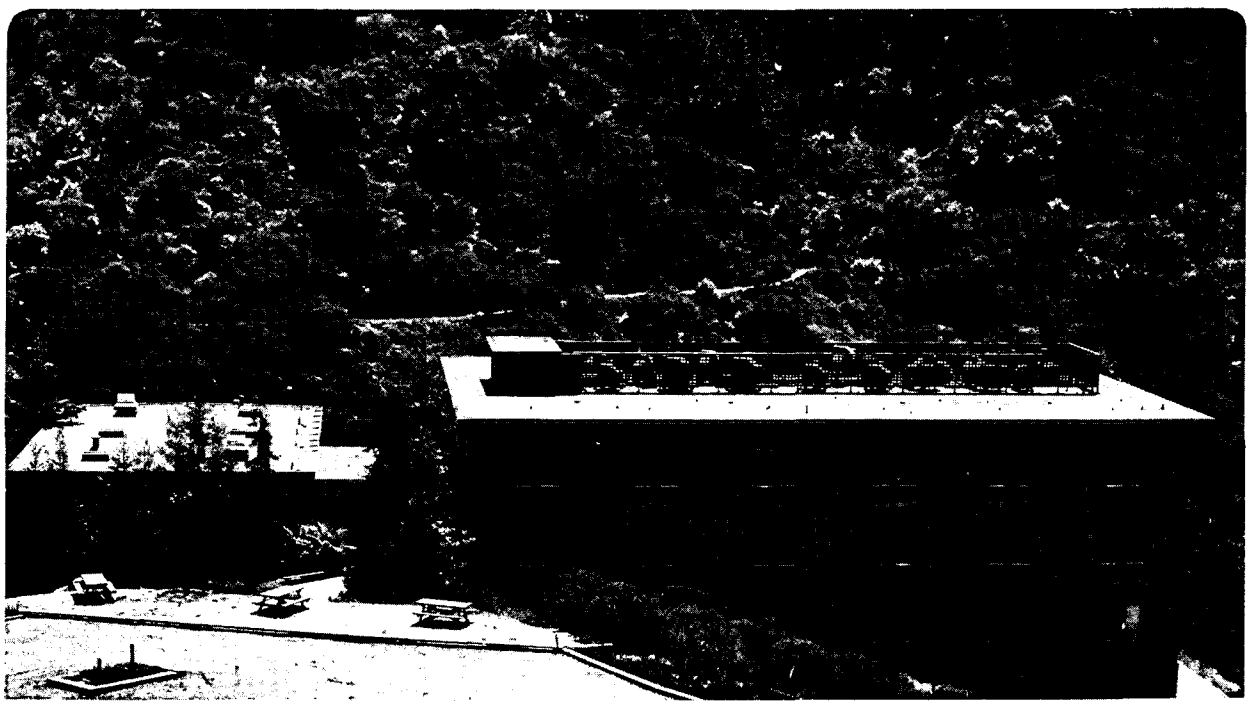

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Structure Determination with HREELS and LEED: The Molecular Structure of Chemisorbed Benzene on Pd(111)

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The combination of HREELS (High-Resolution Electron Energy-Loss Spectroscopy) and LEED (Low-Energy Electron Diffraction) has been successfully applied to study complicated coadsorption structures of benzene and CO on various transition metal surfaces. Through these studies, different benzene structures have emerged depending on the substrate metal. Recent work concerns coadsorption of benzene and CO on Pd(111), where an almost *gas—phase like* benzene structure has been detected.

1. Introduction

LEED has already been applied to many clean surfaces and overlayer covered surfaces, and more than 200 such structures have been determined [1]. In 1983, an effective approximation of the theoretical dynamical LEED analysis was proposed [2] for determining organic overlayer structures with any unit cell size. With that method, four structures have been analyzed of benzene coadsorbed with CO on Pt(111) [3], Rh(111) [4,5], and Pd(111) [6]. These may be labeled:

I. Pt(111)-$(2\sqrt{3}\text{x}4)$*rect*-$2C_6H_6 + 4CO$

II. Rh(111)-c$(2\sqrt{3}\text{x}4)$*rect*-$C_6H_6 + CO$

III. Rh(111)-(3x3)-$C_6H_6 + 2CO$

IV. Pd(111)-(3x3)-$C_6H_6 + 2CO$

In all cases, CO was responsible for forming cooperative superlattices of benzene and CO. In the following sections, the procedure of the structure determination and the results for the Pd(111)-(3x3)-$C_6H_6 + 2CO$ system will be described, and then the benzene structures I - IV will be compared.

2. Structure Analysis of Pd(111)-(3x3)-C_6H_6 + 2CO

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). This coadsorbed structure was analyzed using HREELS and LEED.

2.1. Characterization of Surface Species with HREELS

In general, chemical information obtained with non-LEED techniques helps to narrow down the set of structure models that need to be tested by LEED analysis. HREELS [7] is one of the most powerful tools available for this purpose in the case of molecular overlayer. Figure 1 shows a HREEL spectrum taken from a (3x3) structure of coadsorbed benzene and CO [8]. The HREELS for pure benzene on Pd(111) is also shown for comparison. (This spectrum is essentially the same as the spectrum reported by Waddill et al [9]) The 765cm^{-1} peak is due to the γ_{CH} mode of benzene (out of plane CH bending), and the 1735cm^{-1} peak is due to the C-O stretching mode. The spectrum for the (3x3) structure implies the following:

1. Both benzene and CO are adsorbed molecularly.
2. The very weak in-plane modes and strong γ_{CH} mode of benzene indicate that the benzene molecules lie parallel to the surface (according to the surface dipole selection rule [7]).
3. The disappearance of the 815cm^{-1} peak, which is seen in the pure benzene spectrum on Pd(111) [9], may indicate the benzene switches to a site with different symmetry by coadsorbing with CO. (For pure benzene on Pd(111), bridge site adsorption has been proposed by Waddill et al. [9])
4. The C-O stretching frequency is such that the CO molecules are most likely bonded at three-fold hollow sites.

These HREELS results, together with thermal desorption yields of CO and knowledge of the Van der Waals radii of each molecule, lead to the structure model as shown in Figure 2. The number of benzene and CO molecules within each (3x3) unit cell is thereby set to one and two, respectively.

2.2. Dynamical LEED Analysis

Theory and experiment of LEED are described in references [10] and [11]. In our analyses, the following structural parameters were varied .

1. For Pd(111) substrate: substrate relaxation between the 1st and 2nd layer.
2. For CO: adsorption site, C-O bond length, and Pd-C bond length. (Upright CO is assumed based on the HREELS data.)
3. For benzene:, adsorption site, azimuthal orientation angle with respect to the substrate, Pd-C separation, and in-plane benzene ring distortion of the Kekulé type.

In total, approximately 1500 distinct structures were examined. The theoretical I-V curves for these structural models were compared with experimental I-V curves quantitatively using R-factors. The best structure for Pd(111)-(3x3)-C_6H_6 + 2CO is illustrated in Figure 3. 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, given the uncertainty of about 0.10Å in the C-C bond lengths determination.

3. Comparison of Benzene Structures on Pd(111), Rh(111), and Pt(111).

In Table 1, the benzene structures on Pd(111), Rh(111), and Pt(111) are shown. The benzene-transition metal interaction can be understood in the framework of d-π interactions as in coordination chemistry. These interactions decrease net C-C bond order of the benzene ring, and can result in the benzene ring expansion. 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 γ_{CH} mode increases from Pd(111) to Rh(111) to Pt(111) [8,9,12,13,14].

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.

4. Implication to Acetylene-Benzene Interconversion

When the surface benzene-metal complex is heated, desorption of molecular benzene competes with the benzene decomposition pathway on these three surfaces. Koel et al [15] have proposed, based on TDS (Thermal Desorption Spectroscopy) and HREELS, that benzene decomposes on Rh(111) through an acetylene-like intermediate. Interestingly, on supported Rh particles, benzene to acetylene conversion occurs with coadsorbed CO [16]. These may be related to the strong metal-benzene interactions and the Kekulé type distortion of benzene molecules observed on Rh(111) surface.

It is well known that Pd(111) surface can catalyze acetylene to benzene conversion under UHV conditions.[17-22] (This reaction does not occur on Rh(111) or Pt(111).) 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. Weak benzene-metal interaction is not, of course, a sufficient condition to form benzene from acetylene. For example Ag(111) can not catalyze this reaction even though benzene-metal interaction is much weaker on this surface. The acetylene needs to intact sufficiently strongly with the metal to start the reaction.

5. Conclusions

An ordered (3x3) benzene overlayer was formed on Pd(111) by coadsorbing benzene and CO. The surface structure was determined by combining LEED and HREELS. No molecular distortion has been detected for benzene on Pd(111) within the error bar. Instead, large benzene-metal separation has been detected. A trend toward more distortion can be seen in going from Pd(111) to Rh(111) to Pt(111), while the metal-carbon bond lengths decrease in that sequence.

Acknowledgements

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Figure captions

1) Top: High Resolution Electron Energy Loss Spectrum (HREELS) of Pd(111)-(3x3)- C_6H_6+2CO.

   bottom: HREELS of disordered C_6H_6 on Pd(111).

2) The structure model of Pd(111)-(3x3)-C_6H_6+2CO obtained with HREELS and TDS. (Bond lengths, bond angles etc. are not yet determined.)

3) The final structure for Pd(111)-(3x3)-C_6H_6+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 overlayer and coadsorbed superlattices with CO.

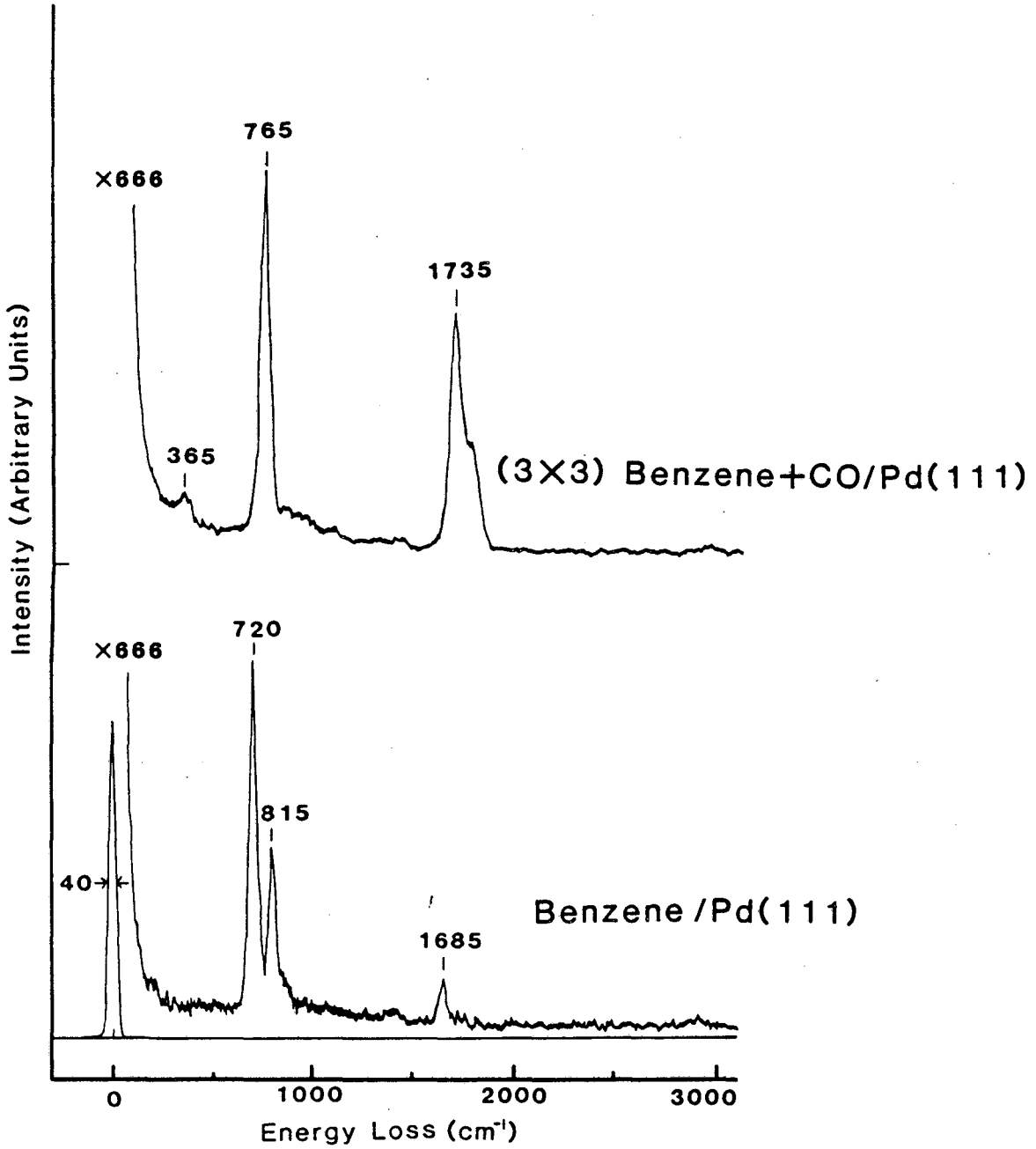

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Fig. 1

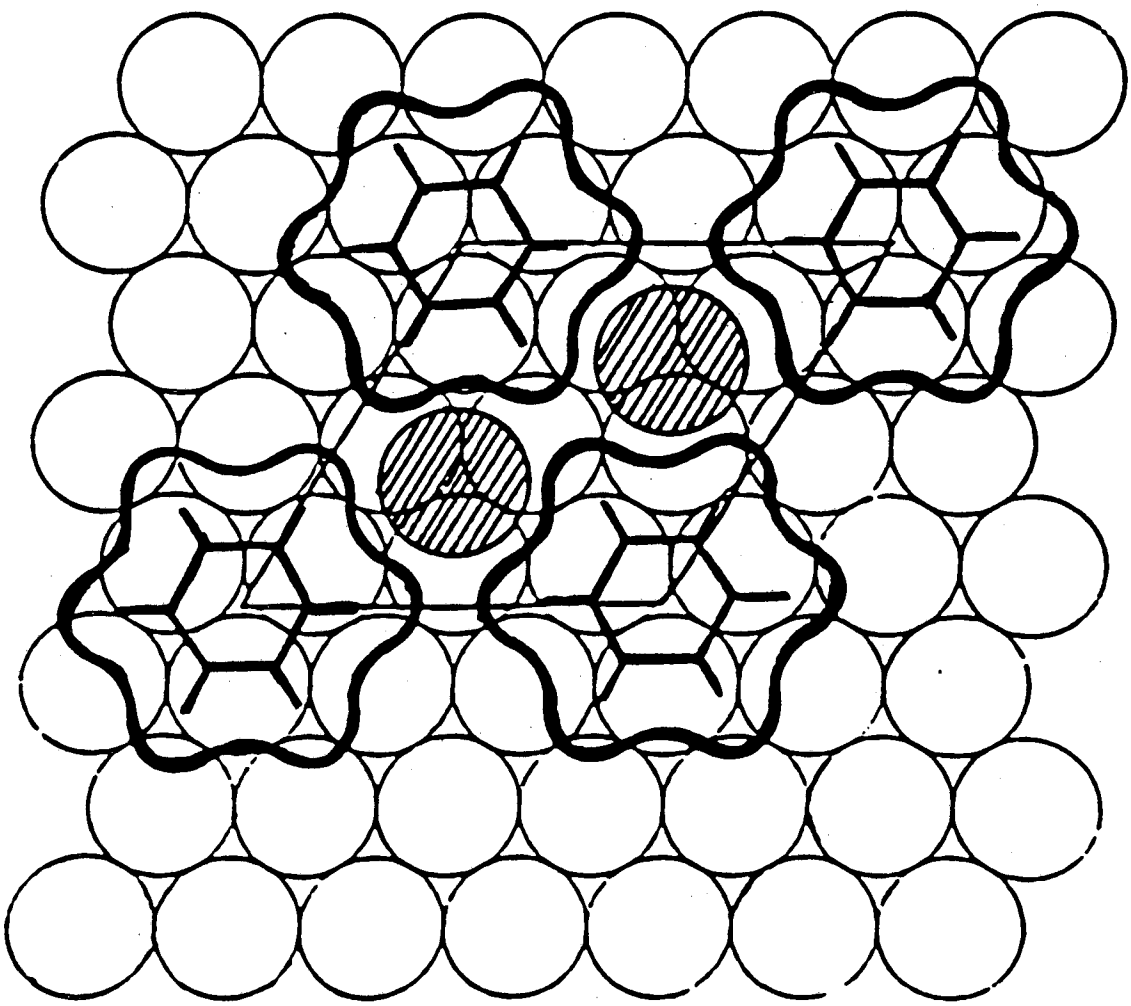

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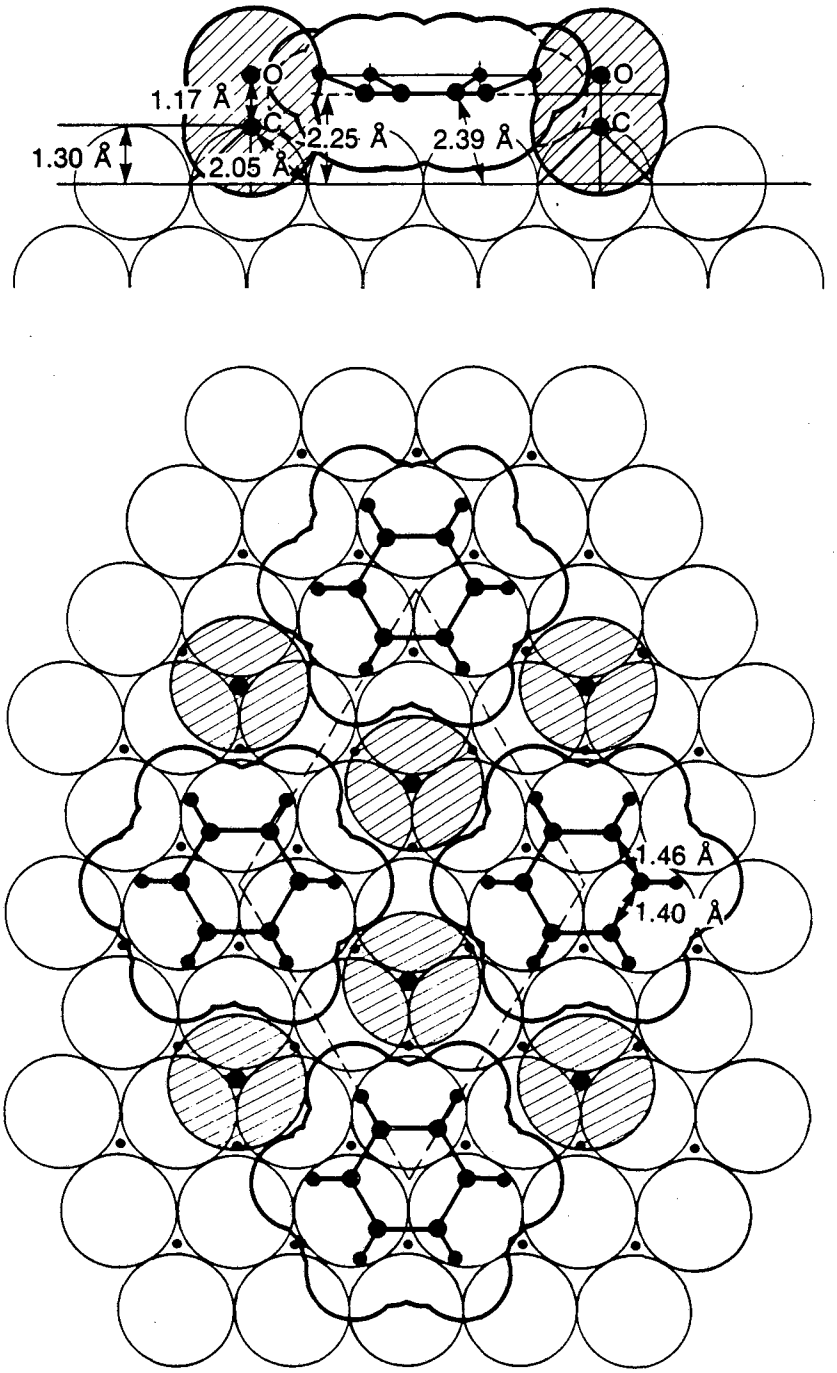
Fig. 2



Pd (111) – (3 × 3) – C_6H_6 + 2CO

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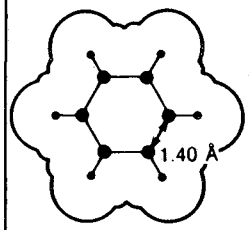
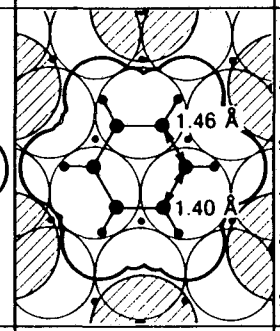
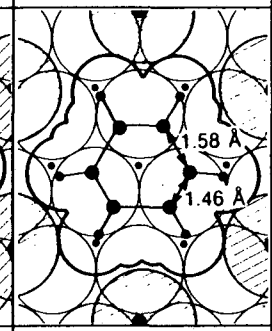
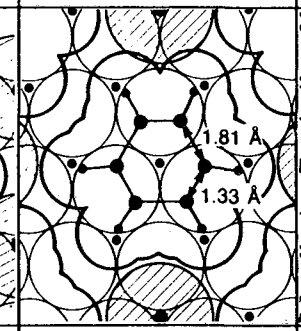
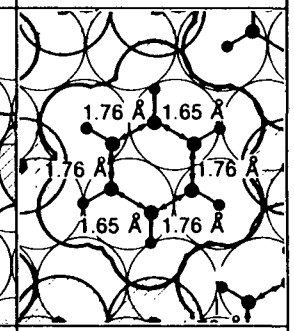
Fig. 3

Substrate	(Gas Phase)	Pd(111)	Rh(111)		Pt(111)
Surface Structure		(3x3)-C_6H_6 + 2CO	(3x3)-C_6H_6 + 2CO	c($2\sqrt{3}$x4)rect-C_6H_6 + CO	($2\sqrt{3}$x4)rect-2C_6H_6 +4CO
The Structure of Benzene					
C_6 Ring Radius (Å)	1.40	1.43±0.10	1.51±0.15	1.65±0.15	1.72±0.15
d_{M-C}(Å)	-	2.39±0.05	2.30±0.05	2.35±0.05	2.25±0.05
$\gamma_{CH}(cm^{-1})$*	670	720-770	780-810		830-850

XBL 878-3565

Table 1

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