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### Authors

Mate, CM.  
Somorjai, G.A.

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C.M. Mate and G.A. Somorjai

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CARBON MONOXIDE INDUCED ORDERING OF BENZENE ON PT(111) AND RH(111)  
CRYSTAL SURFACES

C. M. Mate and G. A. Somorjai

Materials and Molecular Research Division and Department of Chemistry  
University of California  
Berkeley, California 94720

ABSTRACT

Carbon monoxide induced ordering of an organic molecule, benzene, has been studied on the Pt(111) and Rh(111) crystal surfaces using low-energy electron diffraction, high-resolution electron energy loss spectroscopy, and thermal desorption spectroscopy. We propose detailed geometries for all the ordered structures of coadsorbed CO and benzene. Ordering in the adsorbed overlayer is proposed to result from the interactions between adsorbed CO molecules in the presence of benzene.

## 1. Introduction.

In recent years, crystallography by low-energy electron diffraction (LEED) has been a very successful technique for determining the surface structure of ordered monolayers of small molecular adsorbates on single crystal surfaces [1]. However, surface structure determination of larger organic molecules by LEED has been limited since these organic adsorbates frequently do not form ordered overlayers readily on surfaces. Although a new method has recently been proposed [2] for using LEED to determine the structure of disordered overlayers, LEED crystallography of ordered overlayers will probably remain the more practical way of determining the structure of adsorbates on surfaces.

This paper reports how a particular organic adsorbate, benzene, can be induced into several ordered lattices by the coadsorption with CO on the Pt(111) and Rh(111) crystal surfaces. On Pt(111), ordering in the adsorbed benzene layer does not occur in the absence of coadsorbed CO. Therefore, CO-induced ordering should enable us to determine the surface structure of benzene on Pt(111) by a dynamical LEED analysis. On Rh(111), benzene orders at saturation coverage without coadsorbed CO, but orders differently with coadsorbed CO. The formation of CO-induced ordered structures on both Pt(111) and Rh(111) illustrates that this effect is not restricted to one adsorbate-metal system. CO-induced ordering of benzene on these surfaces can be explained by the interactions between adsorbed CO molecules in the presence of coadsorbed benzene. Therefore, by coadsorbing an ordering agent such as carbon monoxide with organic adsorbates, it should become possible to determine the structure of the resulting ordered overlayers by a LEED analysis.

The ordered structures of CO and benzene on Pt(111) and Rh(111)

were studied using low-energy electron diffraction (LEED), high-resolution electron energy loss spectroscopy (HREELS), and thermal desorption spectroscopy (TDS). From the LEED patterns, the periodicity and symmetry of the ordered structures are deduced. The integrity and orientation of the CO and benzene within the ordered structures are determined from HREELS spectra. The relative coverages of CO and benzene within the various unit cells are determined by TDS. Using the information obtained from these three techniques, we propose detailed geometries for the ordered structures of benzene and benzene plus CO on Pt(111) and Rh(111).

Within these structures, we find that CO molecules prefer to adsorb at bridge and hollow sites rather than at top sites as on clean Pt(111) and Rh(111) surfaces. This shift in CO sites can result from both blocking of top sites by benzene molecules and charge transfer via the substrate to the  $2\pi^*_{CO}$  orbital. We also find that benzene adsorbed on Rh(111) shifts from bridge to hollow sites when coadsorbed with CO.

## 2. Experimental.

Our experiments were conducted in a ultra-high vacuum chamber which was equipped for LEED, Auger-electron spectroscopy, TDS, and HREELS. Our HREEL spectrometer is similar to other designs in use [3]. The spectrometer was operated at an overall system resolution between 5 meV and 7.5 meV ( $40\text{ cm}^{-1}$  and  $60\text{ cm}^{-1}$ ) and with an incident beam energy of 5 eV. The platinum and rhodium surfaces were cleaned by cycles of  $\text{Ar}^+$  sputtering,  $\text{O}_2$  treatments, and annealing in vacuum at 1200 K. Surface cleanliness was monitored by Auger-electron spectroscopy and HREELS. During experiments, the background pressure in the chamber was typically  $1 \times 10^{-10}$  torr.

### 3. Results.

#### 3.1 CO/C<sub>6</sub>H<sub>6</sub>/Pt(111).

The adsorption of benzene on Pt(111) has been studied by several researchers [4,5,6]. Gland and Somorjai reported in 1973 the observation of two LEED patterns [4], which can be labeled  $(2\sqrt{3}\times 4)\text{rect}$  and  $(2\sqrt{3}\times 5)\text{rect}$ , after exposing a Pt(111) surface to large doses of benzene ( $>50\text{L}$ ). The notation  $(2\sqrt{3}\times 4)\text{rect}$  means that the overlayer orders in a rectangular superlattice and the lattice spacing is  $2\sqrt{3}$  by 4 times the substrate nearest neighbor distance. We were able to reproduce the two LEED structures reported by Gland by similar large exposures of benzene. HREEL spectra, however, indicated a significant amount of CO had coadsorbed on the surface from the vacuum background gases during the large exposures to benzene. We were also able to form these LEED structures by simply adding CO to a Pt(111) surface precovered with a disordered saturation coverage of benzene. CO exposures between 0.1L and 0.5L induced a well ordered  $(2\sqrt{3}\times 4)\text{rect}$  pattern (1 Langmuir =  $10^{-6}$  torr·s). Between 0.5L and 1.0L of CO, the LEED pattern transformed from a  $(2\sqrt{3}\times 4)\text{rect}$  pattern to  $(2\sqrt{3}\times 5)\text{rect}$  pattern by a continual splitting of the LEED spots. Continued exposure of the  $(2\sqrt{3}\times 5)\text{rect}$  structure to CO gas eventually caused it to disorder after 5L CO and completely displaced benzene from the Pt(111) surface after 20L. During our experiments, no LEED patterns of benzene on Pt(111) were observed without coadsorbed CO except for a disordered ring pattern at saturation coverage similar to that observed by other workers [4,5].

Fig. 1 shows vibrational spectra obtained by HREELS in the specular direction for a disorder monolayer of pure benzene on Pt(111) and for the the two different ordered monolayers of CO coadsorbed with a saturation

coverage of benzene. In these experiments, the Pt(111) sample was maintained at 300 K during the adsorption of benzene and carbon monoxide and then cooled to 77 K during the HREELS measurements. HREEL spectra taken at 300 K are the same as those at 77 K in Fig. 1 except in the C-O stretching region. At 300 K, the loss at  $\sim 2030 \text{ cm}^{-1}$  does not occur for CO exposures less than 1.5L, and the two losses at  $\sim 1700 \text{ cm}^{-1}$  and  $\sim 1800 \text{ cm}^{-1}$  appear as one broad loss. The LEED patterns do not change when the sample is cooled from 300 K to 77 K except for a reduction in background intensity.

The assignment of the vibrational frequencies for benzene chemisorbed on Pt(111) is given in Table 1. This assignment differs slightly from that of Lehwald et al [5] where the loss at  $\sim 1420 \text{ cm}^{-1}$  was assigned to the  $\nu_9$  of benzene. Our assignment, however, is consistent with more recent studies of benzene on other metal surfaces [9,10,11]. The difference in assignment does not change the conclusion that benzene bonds to Pt(111) with its ring oriented parallel to the surface as indicated by the the intense out-of-plane C-H bending mode ( $\gamma_{\text{CH}}$ ) and the weak in-plane modes in the vibrational spectra.

When CO is coadsorbed with benzene on the Pt(111) surface, the vibrational spectra in Fig. 1 clearly show the following. 1) The orientation and bonding of the benzene molecules on the surface do not change significantly when coadsorbed with CO. 2) CO is adsorbed in three different types of sites. The sites where most of the CO is adsorbed (those with CO modes at  $\sim 1700 \text{ cm}^{-1}$  and  $\sim 1800 \text{ cm}^{-1}$ ) are most likely located within the ordered lattice. The CO mode at  $\sim 2030 \text{ cm}^{-1}$  is probably due to a small amount of CO adsorbing from the CO background pressure during cooling of the sample onto bare top sites outside the



ordered lattice since this mode was not observed in the HREEL spectra of the ordered structures taken at 300 K.

We have observed in agreement with other researchers [12] the extinction of certain spots within the LEED patterns revealing the presence of glide plane symmetries. This symmetry means the ordered structures can be transformed back into themselves by a reflection through the glide plane followed by a translation of half a lattice spacing along the direction of the plane. In order to satisfy this symmetry requirement, the number of molecules per unit cell adsorbed at a particular type of site must be even. Consequently, there should be two benzene molecules per unit cell since the unit cells are not large enough to accommodate more than two flat lying benzene molecules. Also, there should be a minimum of four CO molecules per unit cell since the HREEL spectra indicate that CO is adsorbed at two different types of sites within a unit cell. By comparison of the thermal desorption yield of CO when coadsorbed with benzene to that of the  $c(4 \times 2)$  structure of CO on Pt(111) [13,14], we determined that there are four CO molecules per  $(2\sqrt{3} \times 4)$  rect unit cell and six CO molecules per  $(2\sqrt{3} \times 5)$  rect unit cell.

The glide plane symmetries also help us to deduce the bonding sites of benzene and CO within the ordered structures. Benzene adsorption at top sites or at threefold hollow sites is highly unlikely since adsorption at these sites in an arrangement that also satisfies the glide plane symmetries would result in substantial overlap of the flat lying benzene molecules. Consequently, we conclude that benzene adsorbs at bridge sites since these sites enable the benzene molecules to lie flat and to satisfy the glide plane symmetries without significant overlap between neighboring molecules. We were able to find only a few

ways to arrange the correct number of CO molecules in two kinds of sites along with two flat lying benzene molecules within the  $(2\sqrt{3}\times 4)$ rect and  $(2\sqrt{3}\times 5)$ rect unit cells and still satisfy the observed glide plane symmetries. The arrangements we prefer are shown in Figs. 2A and 2B. The high packing density of molecules follows from the glide plane symmetries and from the measurements of surface coverage by thermal desorption yields. The losses at  $\sim 1700\text{ cm}^{-1}$  and  $\sim 1800\text{ cm}^{-1}$  in the HREEL spectra are assigned to C-O stretching frequencies of CO adsorbed respectively at hollow sites and bridge sites within the proposed structures.

### 3.2 CO/C<sub>6</sub>H<sub>6</sub>/Rh(111).

Like benzene adsorbed on Pt(111), different LEED patterns were observed for benzene on Rh(111) at 300 K depending on the coverage of coadsorbed CO. On a Rh(111) surface with no CO adsorbed, benzene orders in a  $(2\sqrt{3}\times 3)$ rect lattice at saturation coverage. When benzene and CO are coadsorbed, we observed depending on CO coverage two new and different ordered structures which can be labeled  $c(2\sqrt{3}\times 4)$ rect and  $(3\times 3)$ . These LEED structures have been reported previously [9,12,15], but the authors did not realize at the time how important CO impurities from the background pressure ( $\sim 5\times 10^{-10}$  torr) were in ordering the structures.

We were able to observe the CO-benzene LEED patterns most readily when the rhodium surface, at 300 K, was first precovered with a coverage of CO and then exposed to 5L of benzene, an amount sufficient to saturate the surface. In Fig. 3, the closed circles give the benzene and CO coverages when the surface was exposed to CO and benzene in this manner. The open circles in Fig. 3 represent experiments where the surface, predosed with CO, was exposed to the minimum amount of benzene for which LEED patterns were observed. The similarity of the results for a minimum

benzene exposure to that of a saturation exposure indicates that ordering of coadsorbed CO and benzene occurs when the surface coverage is close to saturation.

For Fig. 3, the coverages of CO and benzene were determined by comparison of the CO and D<sub>2</sub> thermal desorption yields to those of LEED structures that occur over a narrow range of coverages. Benzene-d<sub>6</sub> (C<sub>6</sub>D<sub>6</sub>) was used in these experiments to minimize the effect of the hydrogen background pressure on the results. The CO desorption yields were compared to that of the ( $\sqrt{3}\times\sqrt{3}$ )R30° structure of pure adsorbed CO on Rh(111) [15,16]. Benzene-d<sub>6</sub> coverages were determined by comparing the D<sub>2</sub> desorption yield to that of the ( $2\sqrt{3}\times 3$ )rect benzene-d<sub>6</sub> structure. For the benzene coverages, we assume that there are two benzene molecules per ( $2\sqrt{3}\times 3$ )rect unit cell and that the D<sub>2</sub> desorption yield is proportional to the benzene-d<sub>6</sub> coverage since less than two percent of the benzene desorbs molecularly from Rh(111) [9]. CO and benzene coverages are defined as the ratio of adsorbed molecules to surface atoms.

Figs. 4A and B show thermal desorption spectra for CO and D<sub>2</sub> when 5L of benzene-d<sub>6</sub> is coadsorbed with CO on Rh(111) along with the thermal desorption spectra for CO and benzene-d<sub>6</sub> adsorbed alone on Rh(111). The thermal desorption spectra show that benzene decomposition and CO desorption both occur ~490 K on Rh(111). These processes continue to occur at this temperature when CO and benzene are coadsorbed.

As shown in Fig. 3, the LEED patterns are observed over a range of coverages indicating the formation of ordered domains. If there is one CO molecule per  $c(2\sqrt{3}\times 4)$ rect unit cell, then domains of this structure should completely cover the surface at a CO coverage of one-eighth

of a monolayer (0.125 monolayer coverage). Since the  $c(2\sqrt{3}\times 4)$ rect LEED pattern was sharpest and most intense at  $\sim 0.12$  of a monolayer of CO, we conclude that there is only one CO molecule per  $c(2\sqrt{3}\times 4)$ rect unit cell. Similarly, we conclude that there are two CO molecules per  $(3\times 3)$  unit cell since the  $(3\times 3)$  LEED pattern was sharpest and most intense at  $\sim 0.22$  of a monolayer of CO.

For the  $(2\sqrt{3}\times 3)$ rect LEED pattern of benzene adsorbed on Rh(111), we observed the extinction of certain spots revealing the presence of a glide plane symmetry for this structure. As for the CO-benzene structures on Pt(111), we conclude from the glide plane symmetry that there are two benzene molecules per unit cell and the benzene molecules are centered over bridge sites. Fig. 5 shows how two benzene molecules can be arranged in a  $(2\sqrt{3}\times 3)$ rect unit cell to satisfy the glide plane symmetry. Rotation of the benzene molecules is also possible but this would result in a slight overlap of neighboring molecules.

Fig. 6 shows HREEL vibrational spectra for the three ordered structures on Rh(111) at 300 K. The assignment of the vibrational frequencies for benzene chemisorbed on Rh(111) is given in Table 1. This assignment has been discussed in a previous paper [9]. When coadsorbed with CO, the spectrum of benzene is essentially unchanged except for small changes in the region of the out-of-plane bending ( $\gamma_{CH}$ ) mode. Fig. 7 shows this region with an expanded scale to illustrate these changes. For the  $(2\sqrt{3}\times 3)$ rect structure, two losses are observed at  $775\text{ cm}^{-1}$  and  $805\text{ cm}^{-1}$  which we interpret as corresponding to the  $\gamma_{CH}$  mode of benzene molecules bonded at two different sites [9]. For the  $c(2\sqrt{3}\times 4)$ rect structure only one  $\gamma_{CH}$  mode at  $775\text{ cm}^{-1}$  occurs indicating benzene

chemisorption at only one site. This mode shifts to slightly higher frequencies with increasing CO coverage to a value of  $805\text{ cm}^{-1}$  for the (3x3) structure.

In the  $(2\sqrt{3}\times 3)$ rect structure shown in Fig. 5, the benzene molecules are adsorbed in only one type of site within the ordered lattice. Two out-of-plane bending modes ( $\gamma_{\text{CH}}$ ), however, are observed in the HREEL spectra of this structure as shown in Fig. 7. We interpret the mode at  $775\text{ cm}^{-1}$  as the  $\gamma_{\text{CH}}$  mode of a small number of benzene molecules adsorbed at three-fold hollow sites and disordered on the surface. The mode at  $805\text{ cm}^{-1}$  is then assigned to the  $\gamma_{\text{CH}}$  of benzene adsorbed at bridge sites within the ordered lattice. As further evidence that a fraction of the benzene molecules is disordered in the  $(2\sqrt{3}\times 3)$ rect structure, we note that the background intensity of the  $(2\sqrt{3}\times 3)$ rect LEED pattern was substantially higher than that for the CO-benzene LEED patterns indicating a fair amount of disorder within the  $(2\sqrt{3}\times 3)$ rect structure.

The spectra in Fig. 6 indicate that CO is bonded at only one site within the ordered CO-benzene structure on Rh(111). This site is most likely a threefold hollow site for the following reasons. 1) The low C-O stretching frequency ( $1655\text{ cm}^{-1}$  to  $1700\text{ cm}^{-1}$ ) is characteristic of that observed for CO bonded to three metal atoms in metal-carbonyl clusters [18]. 2) A previously reported dynamical LEED analysis for the  $c(2\sqrt{3}\times 4)$ rect structure [15], where the authors assumed no CO molecule was present within the unit cell, indicated a structure with an empty threefold hollow site which could accommodate a CO molecule. The same authors have recently repeated this analysis with CO coadsorbed within the unit cell. This analysis, which will be discussed in detail in a separate publication,

confirms that both CO and benzene bond at hollow sites within the  $c(2\sqrt{3}\times 4)\text{rect}$  unit cell. Fig. 2C shows the  $c(2\sqrt{3}\times 4)\text{rect}$  structure, and in Fig 2D, we propose a similar structure for the  $(3\times 3)$  unit cell.

In these figures, the chemisorbed benzene molecules are drawn with the gas phase dimensions of molecular benzene. The dynamical LEED analysis of M. A. Van Hove et al. [15] indicates, however, a considerable planar distortion of the benzene ring within the  $c(2\sqrt{3}\times 4)\text{rect}$  structure.

The benzene molecules in the other structures in Figs. 2 and 5 may also be distorted away from the gas phase configuration of benzene shown in these figures. Even though chemisorbed benzene may be distorted, we are still able to assign the observed vibrational modes to those of gas phase benzene indicating the molecule is still intact on the surface.

#### 4. Discussion.

##### 4.1 Ordering of Coadsorbed CO and Benzene.

The coadsorption of CO with benzene strongly promotes ordering of the organic molecule into a two-dimensional structure. This somewhat unexpected finding indicates that there are interactions between the coadsorbed molecules on the transition metal surface. These interactions must be weak when compared to the adsorbate-metal interaction since the vibrational and thermal desorption spectra of benzene do not change significantly when coadsorbed with CO.

Theoretical calculations of the interaction between chemisorbed atoms or molecules have shown that adsorbate-adsorbate interactions are generally at least an order of magnitude smaller than the adsorbate-substrate interaction [19]. When the chemisorbed atoms and molecules are separated so that the overlap of adsorbate orbitals is negligible, these calculations have also found that the interaction between adsorbates

are primarily indirect ( i.e., via substrate wavefunctions), oscillate in sign as a function of separation distance, and decrease in magnitude with increasing separation distance. When, these interactions are found to be attractive at certain separation distances, ordered domains can form [19,20].

In our discussion of the interactions responsible for the CO induced ordering of adsorbed benzene, we will mainly consider coadsorbed CO and benzene on Rh(111). In connection with this discussion, we find it useful to refer to the work by E. Ruckenstein and T. Halachev [21] who have used quantum-chemical calculations to study the interaction between CO molecules adsorbed on the Rh(111) surface. These authors considered only interactions occurring through the metal substrate. For two adsorbed CO molecules, these calculations indicate the interaction energy is positive (repulsive) when the CO molecules occupy first nearest neighbor sites and is negative (attractive) when they occupy second and third nearest neighbor sites. In other words, two CO molecules are repelled from sites separated by small distances but are attracted to sites separated by intermediate distances. The observed ordering of the quarter monolayer  $p(2 \times 2)$  CO structure and the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  CO structure [16,17] where CO occupy respectively third and second nearest neighbor sites can then be explained in terms of favorable interaction energies.

Since this kind of interaction between adsorbates has been found in various studies to result in the formation of ordered domains, it is reasonable to propose that the trend in interaction energies ( i.e., positive for CO molecules separated by small distances and negative for CO molecules separated by intermediate distances ) does not change when CO is coadsorbed with benzene. This trend can also explain the observed

dependence of the LEED patterns on the CO and benzene coverages.

As shown in Fig. 3, the  $c(2\sqrt{3}\times 4)$ rect LEED pattern is observed for CO coverages ranging from 0.05 of a monolayer to 0.12 of a monolayer. Benzene coverages are always close to saturation. If one assumes there is only one CO molecule per unit cell, then at 0.05 monolayer of CO coverage, the observation of a  $c(2\sqrt{3}\times 4)$ rect pattern implies that about half of the surface is covered with domains of the  $c(2\sqrt{3}\times 4)$ rect structure. The adsorption of CO within domains at this low coverage is possible if the interaction energy between CO molecules within a  $c(2\sqrt{3}\times 4)$ rect lattice is more negative than when spread uniformly over the surface.

Fig. 3 shows that the  $(3\times 3)$  pattern is observed for CO coverages ranging from 0.22 of a monolayer to 0.44 of a monolayer. If one assumes one benzene molecule and two CO molecules per unit cell, then the observation of a  $(3\times 3)$  pattern over this wide range of CO coverages indicates the formation of domains. Assuming all the benzene is adsorbed within the  $(3\times 3)$  domains, we estimate the CO concentration in regions outside the  $(3\times 3)$  domains to be close to the saturation concentration of CO that occurs at 0.75 of a monolayer. If CO is arranged within the  $(3\times 3)$  unit cell as shown in Fig. 2D, the CO molecules would form a  $(\sqrt{3}\times \sqrt{3})R30^\circ$  lattice with one third of the sites occupied by benzene molecules forming the  $(3\times 3)$  superlattice. Therefore, the interaction between CO molecules should be attractive in this structure. Outside of the domains, the CO molecules should have a repulsive interaction because the high concentration of CO in this region results in the molecules occupying nearest neighbor sites. The CO molecules can then lower their energy by occupying sites within the  $(3\times 3)$  domains rather than sites outside of the domains. For



the same reason, the adsorption of the benzene molecules within the domains helps to lower the CO-CO interaction energy. Essentially, the (3x3) CO-benzene structure enables the maximum number of CO molecules to have the same CO-CO separation distance as in the  $(\sqrt{3}\times\sqrt{3})R30^\circ$  CO structure on Rh(111).

The preceding arguments show that the interactions that exist between adsorbed CO on clean Rh(111) are sufficient to explain the observed LEED structures for coadsorbed CO and benzene. This does not rule out the possibility that the CO-CO interaction may change somewhat in the presence of coadsorbed benzene; some change is to be expected due to the different CO adsorption site in the coadsorbed structure. We argue, however, that the trend in interaction energies - repulsive for CO molecules separated by small distances and attractive for CO molecules separated by intermediate distances - does not change substantially in the presence of benzene. Also, other interactions such as those between benzene-benzene and CO-benzene are not ruled out and may further stabilize the ordered CO-benzene structures. The benzene-benzene interactions are probably weaker than the CO-CO interactions since, in the absence of CO, only a tightly packed  $(2\sqrt{3}\times 3)$ rect structure detected and no loosely packed ordered benzene structures are observed. An attractive CO-benzene interaction would stabilize ordered structures with CO and benzene intermixed in the unit cell whereas a repulsive interaction would favor segregation. However, the important point is that coadsorbed CO and benzene are likely to form an ordered overlayer since CO readily orders on Rh(111) due to favorable interaction energies. Therefore, it should be possible to order other adsorbed overlayers, which might not otherwise order due to weak adsorbate-adsorbate interactions, by introducing a coadsorbate such as CO which has interactions

strong enough to induce ordering in the overlayers .

The ordered structures of CO and benzene on the Pt(111) surface are other possible examples of this effect. Without any coadsorbate, benzene does not order on Pt(111). Adsorbed CO, however, readily orders on this surface into a variety of structures [13,14]. Coadsorbing CO with benzene results in either the  $(2\sqrt{3}\times 4)$ rect or the  $(2\sqrt{3}\times 5)$ rect ordered structures. If the CO molecules are arranged as shown in Figs. 2A and 2B, then the CO-CO separation distance in these CO-benzene structures is nearly the same as that in the  $c(4\times 2)$  structure of CO on Pt(111) [13]. This would support the proposal that CO-CO interactions that ordered CO on a Pt(111) surface persist in the presence of coadsorbed benzene and help order the benzene overlayer.

#### 4.2 Adsorption sites of coadsorbed CO and benzene.

As mentioned earlier, the CO adsorption site changes when benzene is coadsorbed with CO. CO adsorbs preferentially at hollow sites on benzene-covered Rh(111) and at hollow and bridge sites on benzene-covered Pt(111). On initially clean Rh(111) and Pt(111) surfaces, CO chemisorbs first at sites atop of metal atoms [14,17]. Our results suggest two possible causes for the change in CO adsorption sites. 1) When adsorbed at bridge or hollow sites, benzene blocks CO from adsorbing at nearby top sites. 2) Since benzene donates electrons to the metal surface as detected by work function measurements [4], adsorbed benzene could cause CO adsorption at bridge and hollow sites to become energetically more favorable.

Shifts of CO to more highly coordinated adsorption sites have also been observed for CO coadsorbed with alkali atoms, which are also charge donors to the metal surface [22,23,24]. When CO is adsorbed at bridge

and hollow sites, the  $2\pi^*$  orbital of CO has greater overlap with substrate orbitals of the correct symmetry for bonding than when CO is adsorbed at top sites. Consequently, the  $2\pi^*$  CO orbital is able to accept more of the charge donated to the surface by benzene molecules or alkali atoms when CO is bonded at bridge or hollow sites than when bonded at top sites.

Along with the shift in CO adsorption site, a reduction in C-O stretching frequency has also been reported when CO is coadsorbed with alkali atoms [22,23,24]. The reduction in frequency is thought to be caused by charge donation into the anti-bonding  $2\pi^*$  orbital of CO. As shown in Table 2, the C-O stretching frequency for CO bonded to a particular site on a benzene-covered Pt(111) surface is lower than that of CO bonded to an equivalent site on the initially clean surface. The downshift in frequency is generally reduced with an increasing ratio of adsorbed CO molecules to adsorbed benzene molecules. A similar reduction in frequency has been reported for CO coadsorbed with potassium on Pt(111) [23].

There is also a shift in adsorption site for benzene on Rh(111) when it is coadsorbed with CO. As discussed earlier, in the absence of CO, benzene adsorbs at saturation coverage predominantly at bridge sites with a small fraction of the benzene adsorbed at hollow sites. When benzene is coadsorbed with CO in an ordered structure on Rh(111), it adsorbs entirely at threefold hollow sites. As with the shift in CO sites, our results suggest two possible causes for the shift in benzene adsorption site. 1) CO adsorption in hollow sites, which could be caused by charge donation from the benzene to the substrate, blocks benzene adsorption at nearby bridge sites. 2) The electron accepting

properties of CO adsorbed at hollow sites may cause benzene adsorption at hollow sites to become energetically more favorable than at bridge sites.

For benzene on Pt(111), we sometimes observed in the vibrational spectra a shoulder at  $\sim 920 \text{ cm}^{-1}$ . Lehwald et al [5] also observed a loss at  $\sim 920 \text{ cm}^{-1}$  for benzene adsorbed on Pt(111) in the absence of CO. These authors found that the ratio of the intensities of the  $830 \text{ cm}^{-1}$  and the  $920 \text{ cm}^{-1}$  losses changed with benzene coverage and concluded from this that the two losses were from the  $\nu_4$  mode of benzene molecules adsorbed at different types of sites. If this interpretation is correct, then the shoulder at  $\sim 920 \text{ cm}^{-1}$  in our spectra would correspond to a small amount of disordered benzene adsorbed at a site different from the bridge sites in the ordered structures.

Several previous studies of benzene on Pt(111) and Rh(111) surfaces [5,9] have tried to determine the adsorption site symmetry of benzene using HREELS. These studies concluded that the symmetry of adsorbed benzene was  $C_{3v}(\sigma_d)$  since only a small number of benzene modes are observed in the HREEL spectra and those modes that are observed are consistent with a local symmetry of  $C_{3v}(\sigma_d)$ . It was thought that more modes would become dipole active if benzene was bonded to a site of lower symmetry and that these modes would then be observed in the HREEL spectra. The spectra in Fig. 6 illustrate the difficulty, however, in determining the adsorption site of benzene on metal surfaces using only HREELS. There are only small differences in the vibrational spectra of benzene for the  $(2\sqrt{3}\times 3)\text{rect}$  and  $c(2\sqrt{3}\times 4)\text{rect}$  structures even though LEED results indicate that benzene bonds at bridge sites, which have  $C_s$  symmetry, in the  $(2\sqrt{3}\times 3)\text{rect}$  structure and at hollow sites,

which have  $C_{3v}(\sigma_d)$ , in the  $c(2\sqrt{3}\times 4)$ rect structure. This indicates that the metal surface does not significantly distort the benzene molecule from  $C_{3v}$  symmetry or that any distortions do not result in any new dynamic dipole moments perpendicular to the surface.

Recently, Waddill and Kesmodel [25] have suggested that the two losses in the region  $750-950\text{ cm}^{-1}$  can be interpreted as the  $\nu_4$  and  $\nu_{11}$  modes of benzene bonded to bridge site rather than to the  $\nu_4$  mode of benzene bonded to two different types of sites. While this interpretation is consistent with our finding based on LEED results that benzene bonds at bridge sites in certain ordered structures on Pt(111) and Rh(111), it does not rule out the alternate interpretation of two benzene adsorption sites. The work of Waddill and Kesmodel, we believe, further illustrates the difficulty of using HREELS to determine unambiguously the adsorption site of benzene on metal surfaces. LEED, however, is intrinsically a more sensitive technique for determining adsorption sites since it involves electron scattering from both the substrate and adsorbate atoms. Consequently, CO-induced ordering of organic monolayers should be very helpful in determining the structure of organic adsorbates.

##### 5. Conclusions.

Benzene coadsorbed with CO forms a variety of ordered overlayer structures on Pt(111) and Rh(111). In the case of Pt(111), CO-induced ordering of benzene should enable the structure determination of benzene chemisorbed on this surface by a dynamical LEED analysis that would be difficult without the presence of CO since benzene does not order on Pt(111) without CO.

In principle, it should be possible to order any adsorbate by coadsorbing an appropriate ordering agent which has interactions strong

enough to induce ordering. The surface structure of such a molecule, which might not otherwise order, could be determined by LEED crystallography. We are currently attempting to determine whether organic molecules other than benzene would order upon the introduction of coadsorbed carbon monoxide.

#### 6. Acknowledgments.

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Table 1. Assignment of observed vibrational frequencies ( $\text{cm}^{-1}$ ) for benzene chemisorbed on Pt(111) and Rh(111).

Gas phase frequencies[7]	Frequencies of chemisorbed $\text{C}_6\text{H}_6$		Mode type	Mode number[8] and symm. representation	
	on Pt(111)	on Rh(111) ( $2\sqrt{3}\times 3$ )rect			
3062	3000	2970	CH stretch( $\nu_{\text{CH}}$ )	$\nu_1$	$A_{1g}$
673	830	$\sim 805^*$	CH bend( $\gamma_{\text{CH}}$ )	$\nu_4$	$A_{2u}$
1310	1330	1330	ring stretch( $\nu_{\text{CC}}$ )	$\nu_9$	$B_{2u}$
1150	1130	1115	CH bend( $\delta_{\text{CH}}$ )	$\nu_{10}$	$B_{2u}$
1486	1420	1430	ring str.( $\delta_{\text{CC}}$ ) and deform	$\nu_{13}$	$E_{1u}$
--	360	345	M-C stretch( $\nu_{\text{M-C}}$ )		
--	--	545	M-C stretch( $\nu_{\text{M-C}}$ )		

\* Two  $\gamma_{\text{CH}}$  frequencies are observed at  $775 \text{ cm}^{-1}$  and  $805 \text{ cm}^{-1}$  under high resolution.

Table 2. C-O stretching frequencies ( $\text{cm}^{-1}$ ) for CO chemisorbed on clean and benzene covered Pt(111) and Rh(111).

CO site	Pt(111)			Rh(111)		
	clean [14]	( $2\sqrt{3}\times 4$ )rect	( $2\sqrt{3}\times 5$ )rect	clean [22]	c( $2\sqrt{3}\times 4$ )rect	( $3\times 3$ )
hollow	1800	1700	1720	--	1655	1700
bridge	1850	1800	1815	1855	--	--
top	2100	2030	2050	2065	--	--



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## Figure Captions

- Fig. 1. Vibrational spectra for benzene and benzene plus CO adsorbed at 300 K on Pt(111) and then cooled to 77 K.
- Fig. 2. Arrangement of CO and benzene within the ordered structures. As determined by HREELS, benzene is oriented with its ring parallel to the surface and CO (hatched circles) is bonded with its axis perpendicular to the surface. Gas phase Van der Waals dimensions are shown.
- Fig. 3. Benzene coverage versus CO coverage when benzene is coadsorbed with CO. For the (●) circles, the surface was precovered with a given CO coverage then exposed to 5.0L of benzene-d<sub>6</sub>. For the (○) circles, the surface was predosed with a certain CO coverage then exposed to the minimum benzene dose needed to observe a LEED pattern.
- Fig. 4 Thermal-desorption spectra of A) CO and B) D<sub>2</sub> after coadsorbing CO and benzene-d<sub>6</sub> at 300 K on Rh(111).
- Fig. 5. Proposed arrangement of benzene in the (2√3x3)rect unit cell on Rh(111). Gas phase Van der Waals dimensions are shown. The dashed lines indicate the location of the glide planes.
- Fig. 6. Vibrational spectra for benzene and benzene plus CO adsorbed at 300 K on Rh(111).
- Fig. 7. The CH out-of-plane bending mode of benzene is shown with an expanded energy scale for two of the ordered structures on Rh(111).

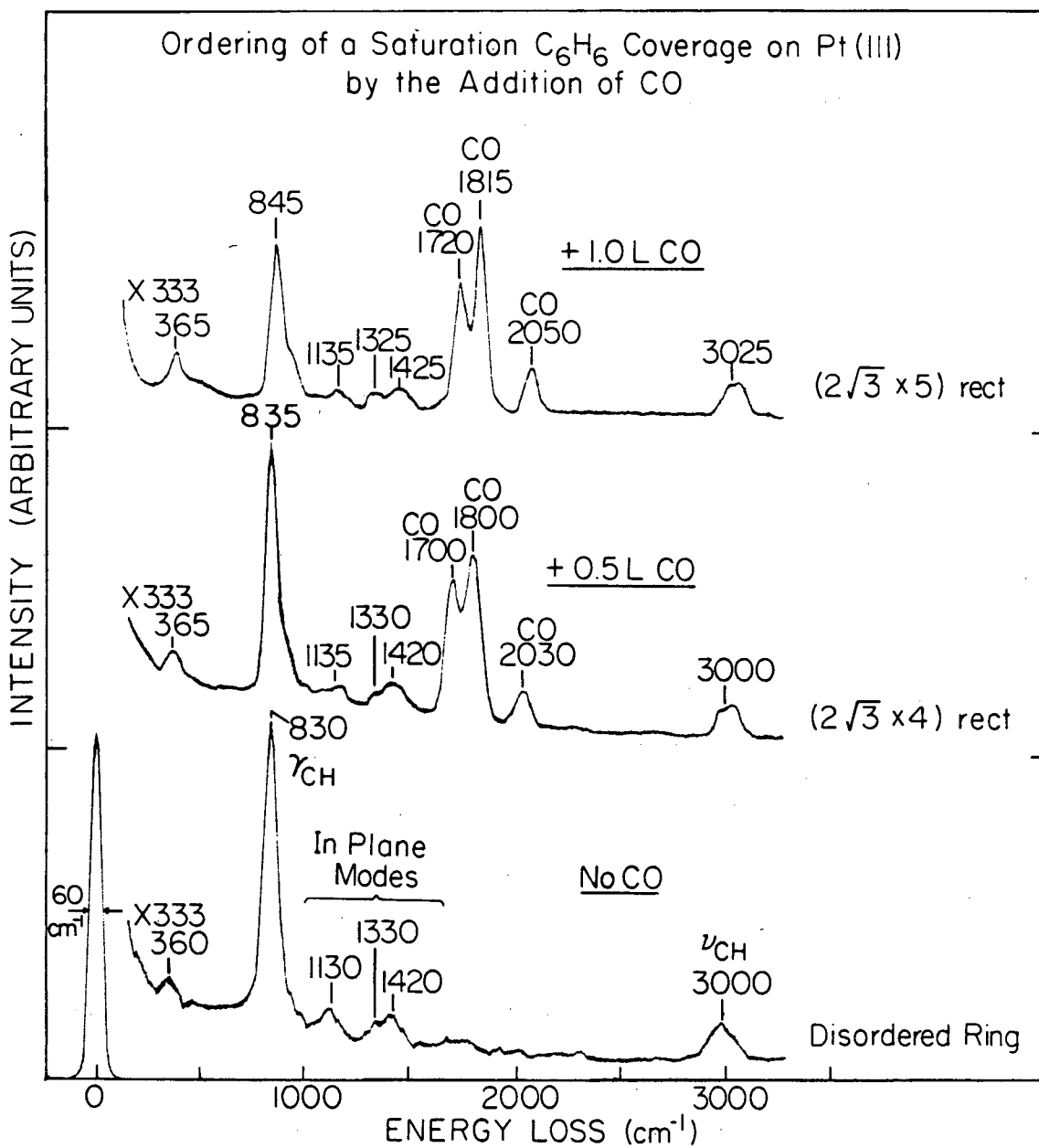
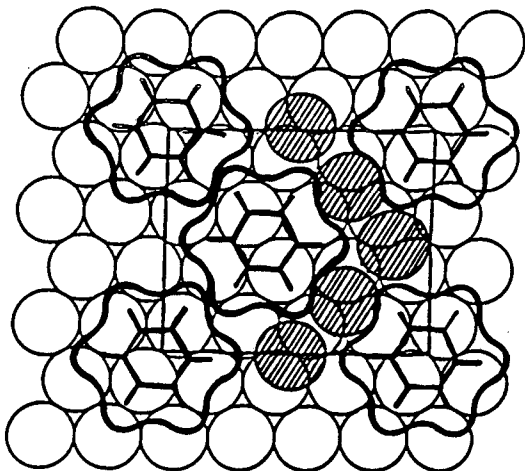


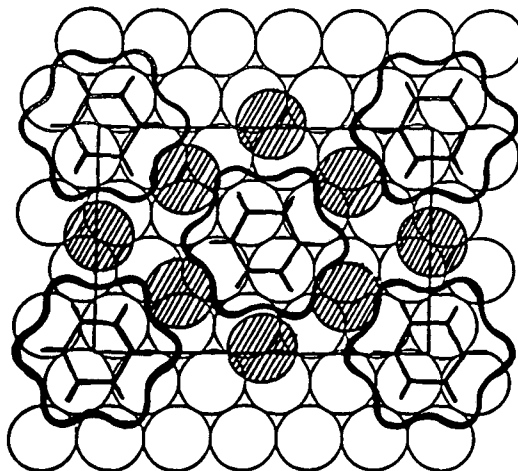
Fig. 1

$$\text{CO/C}_6\text{H}_6/\text{Pt (III)}$$

(A)  $(2\sqrt{3} \times 4)$  rect

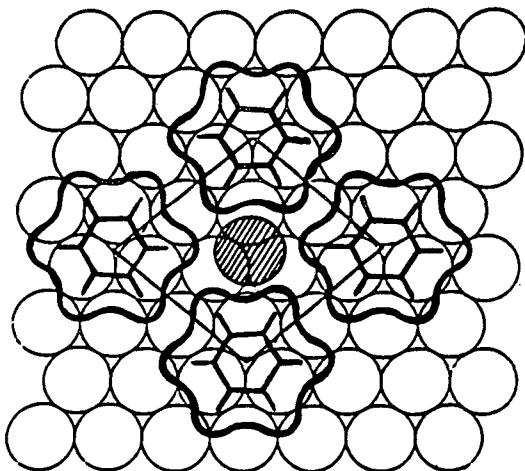


(B)  $(2\sqrt{3} \times 5)$  rect

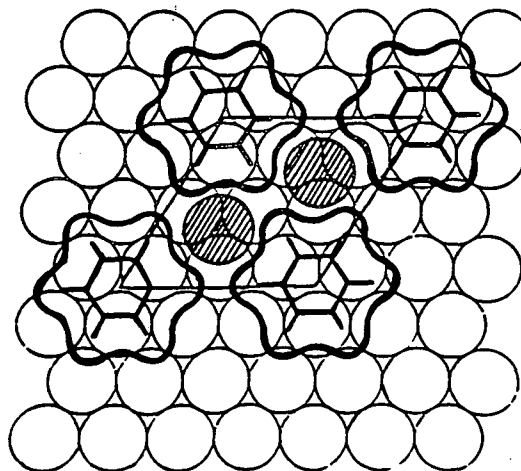


$$\text{CO/C}_6\text{H}_6/\text{Rh (III)}$$

(C)  $c(2\sqrt{3} \times 4)$  rect

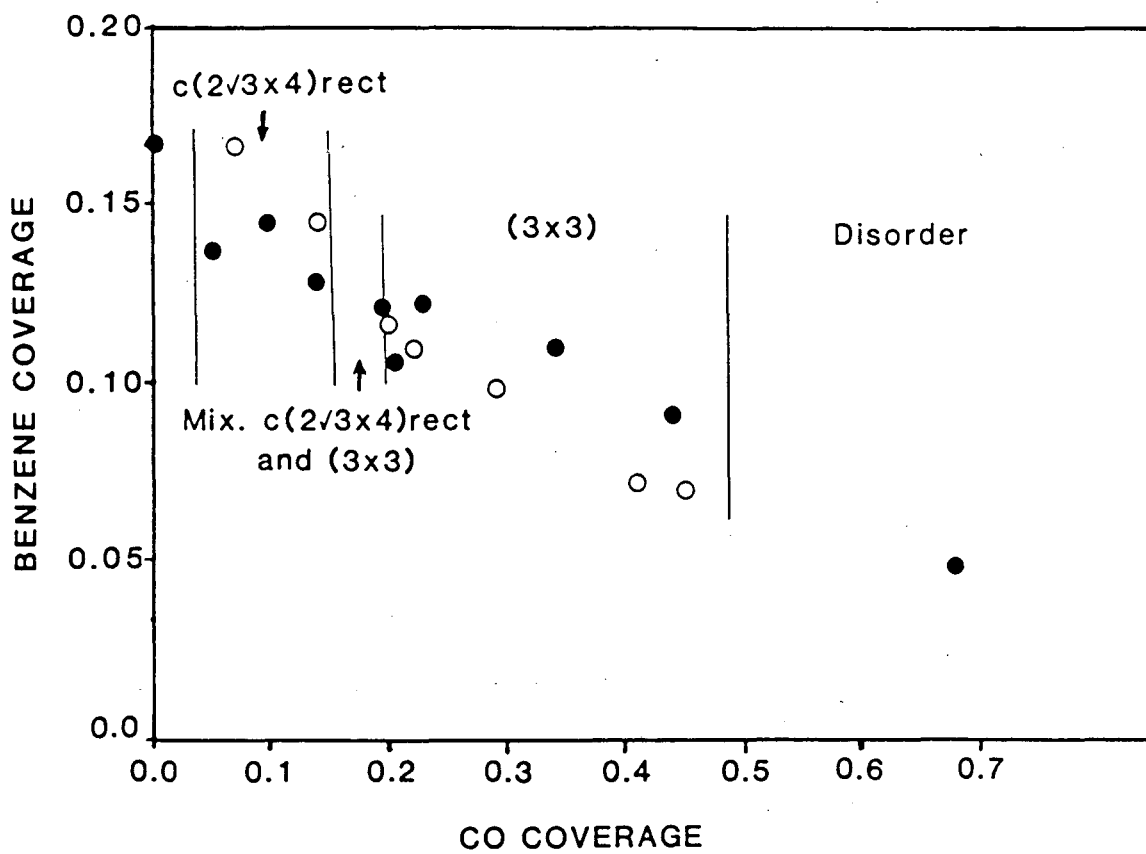


(D)  $(3 \times 3)$



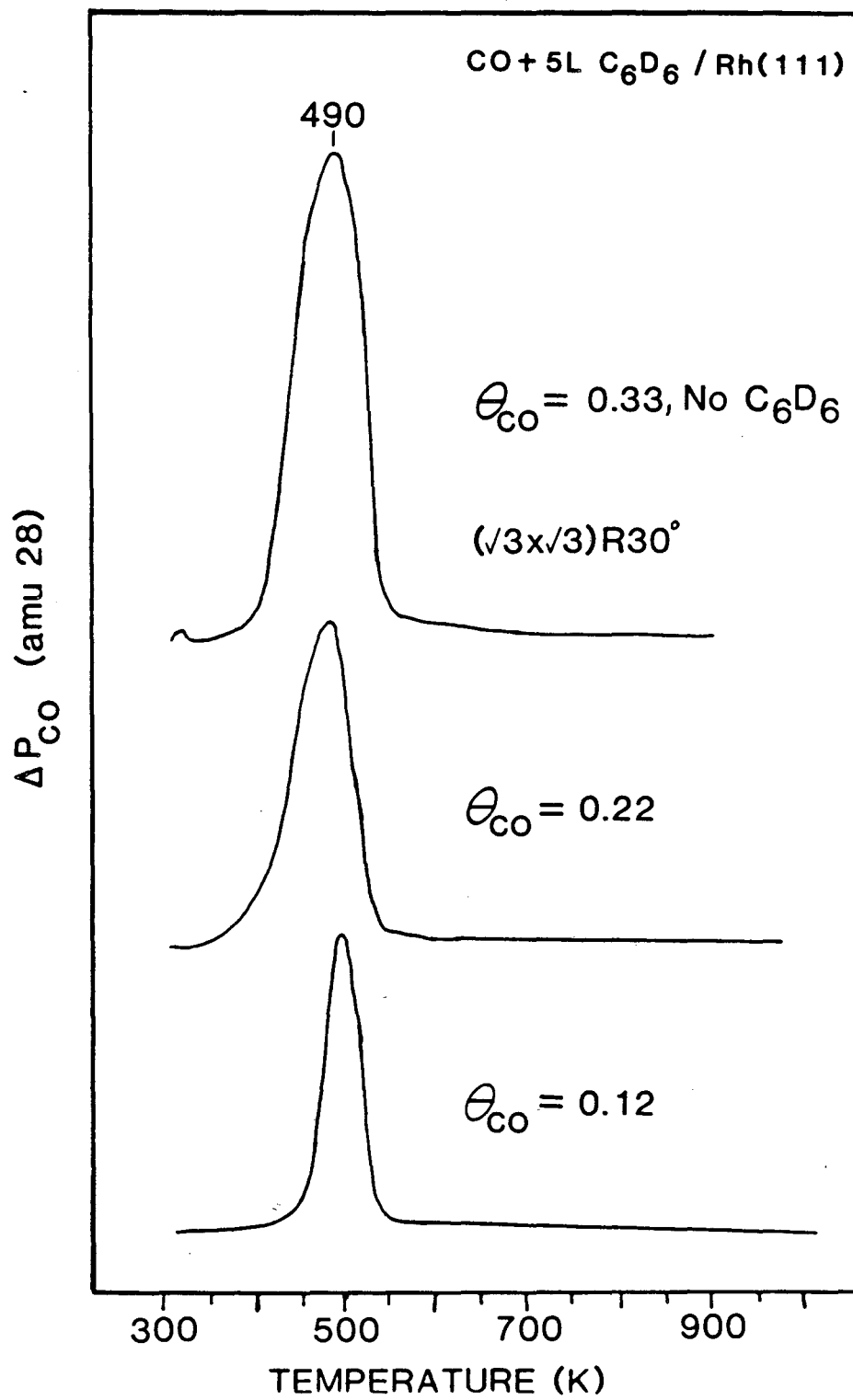
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Fig. 2



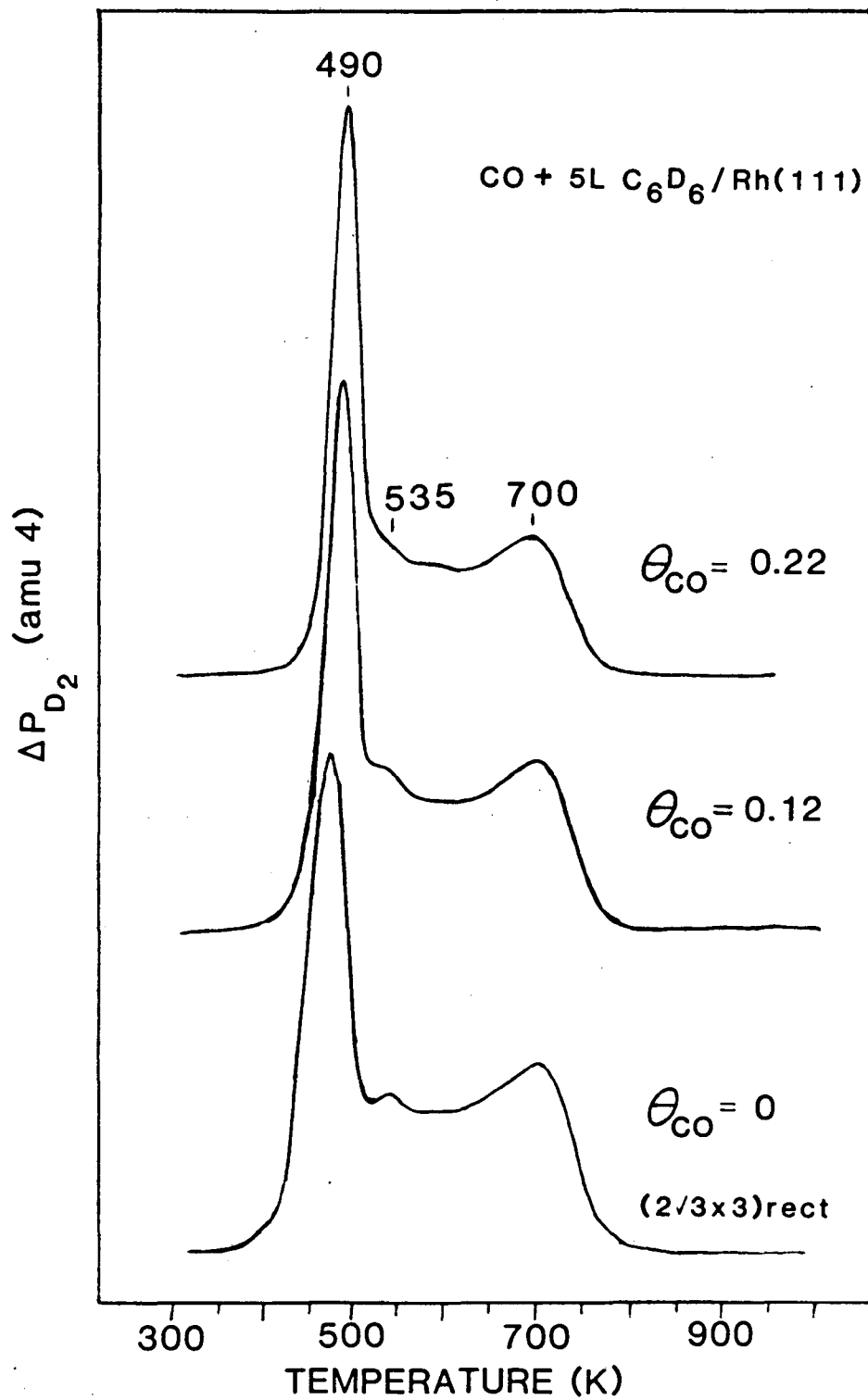
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Fig. 3



XBL 852-1409

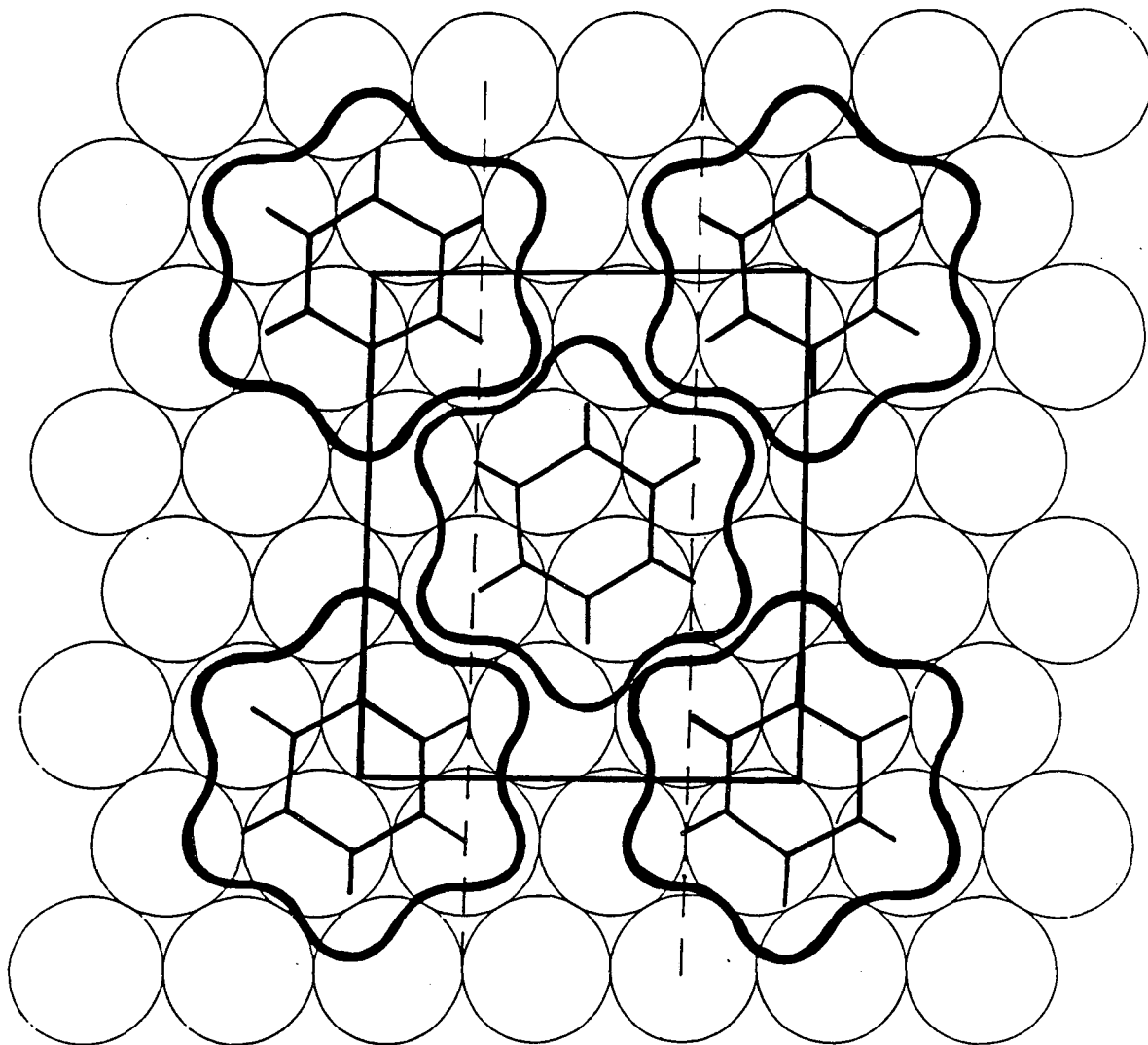
Fig. 4a



XBL 852-1408

Fig. 4b

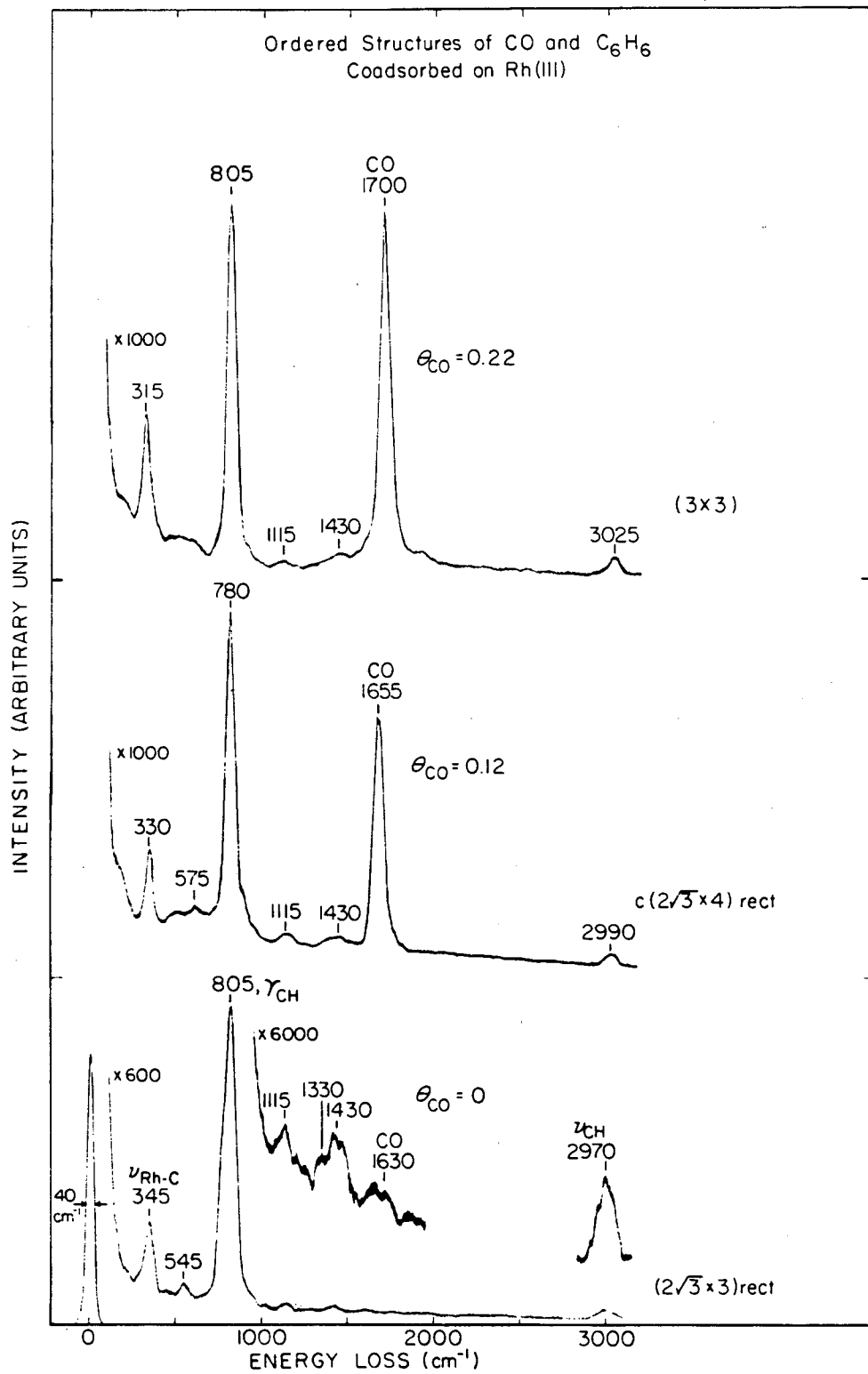




$\text{Rh}(111) + (2/3 \times 3) \text{rect } \text{C}_6\text{H}_6$

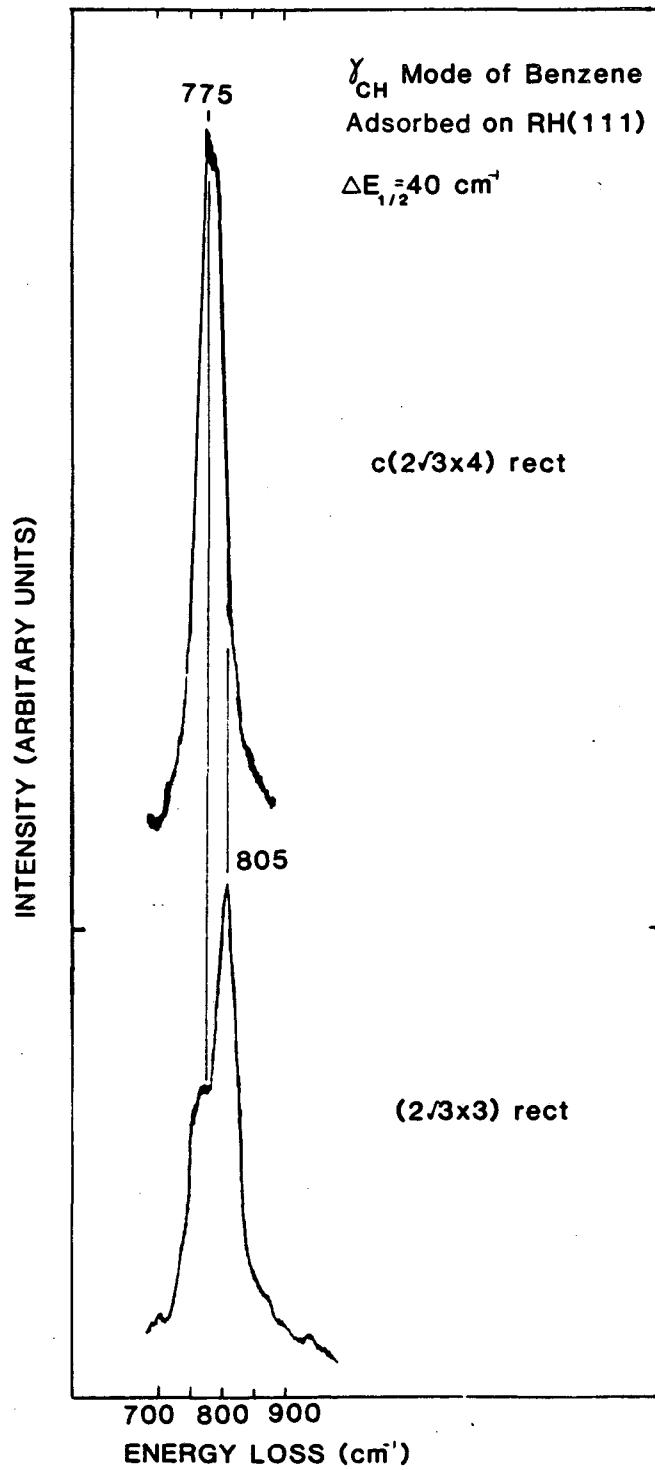
XBL 852-1410

Fig. 5



XBL 849-7383

Fig. 6



XBL 851-1000

Fig. 7

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