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

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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 and high-resolution electron energy loss spectroscopy. We propose detailed geometries for all the ordered structures of coadsorbed CO and benzene. Ordering in the adsorbed overlayer results from the attractive interaction between coadsorbed CO and benzene.

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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 molecular adsorbates on single crystal surfaces [1]. However, structure determination of organic monolayers by LEED has been limited since organic adsorbates frequently do not form ordered overlayers 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 probably will remain the more practical way of determining the structure of adsorbates on surfaces.

This letter 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. 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 invoking an attractive interaction between adsorbed CO and benzene along with the repulsive interactions between adsorbed CO molecules. Therefore, by coadsorbing carbon monoxide with organic adsorbates where an attractive interaction exists, it should become possible to determine the structure by a LEED analysis of the resulting ordered overlayers.

Our experiments were conducted in a ultra-high vacuum chamber which was equipped for LEED, Auger-electron spectroscopy, thermal-desorption

spectroscopy, and high-resolution electron energy loss spectroscopy (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 cm^{-1} and 60 cm^{-1}) and with an incident beam energy of 5 eV. The platinum and rhodium surfaces were cleaned by cycles of Ar^+ sputtering, O_2 treatments, and annealing in vacuum at 900 C. Surface cleanliness was monitored by Auger-electron spectroscopy and HREELS. During experiments, the background pressure in the chamber was typically 1×10^{-10} torr.

The adsorption of benzene on Pt(111) has been studied by several researchers [4,5]. Gland and Somorjai reported in 1973 [4] the observation of two LEED patterns, 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. 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. However, HREEL spectra 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 which had been precovered with a disordered saturation coverage of benzene. A 0.5L CO exposure induced a well ordered $(2\sqrt{3} \times 4)\text{rect}$ pattern and a 1.0L CO exposure induced a well ordered $(2\sqrt{3} \times 5)\text{rect}$ pattern (1 Langmuir = 10^{-6} torr·s). 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 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. Cooling the sample greatly reduced the line widths of the C-O stretching modes as well as the background intensity of the LEED pattern; the spectra remained otherwise unchanged.

The vibrational spectrum of benzene adsorbed on a Pt(111) surface without coadsorbed CO has been discussed previously [5]. The intense out-of-plane C-H bending mode (γ_{CH}) and the weak in-plane modes indicate that benzene bonds to Pt(111) with its ring parallel to the surface. When CO is coadsorbed with benzene on the Pt(111) surface, the vibrational spectra in Fig. 1 clearly show the following. One, the orientation and bonding of the benzene molecules on the surface do not change significantly when coadsorbed with CO. Two, CO is adsorbed in two different types of sites within the ordered lattice. (The CO mode at $\sim 2030\text{ cm}^{-1}$ is due to adsorption from the background CO pressure onto bare top-sites during cooling of the sample and is not present in the ordered structures at 300 K).

If we use information obtained by LEED and by thermal desorption spectroscopy in conjunction with the HREEL spectra, we are able to propose a detailed geometry of the ordered structures of benzene and CO on Pt(111). We have observed in agreement with other researchers [6] 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. The observed glide plane symmetry leads to the conclusion that there are two benzene molecules per unit cell and the benzene molecules are centered on bridge sites. 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) [7], we determined 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 with a possible error of plus or minus one CO molecule per unit cell. However, the number of CO molecules per unit cell must be even to satisfy the glide plane symmetries. For both unit cells, there is only one way to arrange the correct number of CO molecules in two kinds of sites along with two flat lying benzene molecules and still satisfy the glide plane symmetries. These arrangements are shown in Figs. 2A and B.

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. A $c(2\sqrt{3} \times 4)$ rect LEED pattern was observed when the Rh(111) surface was first covered with a one-eighth monolayer of CO (i.e. one CO molecule per eight rhodium atoms) and then exposed to several Langmuirs of benzene. Similarly, a (3×3) LEED pattern was observed after a Rh(111) surface predosed with two-ninths of a monolayer of CO was exposed to several Langmuirs of benzene. These LEED structures have been reported previously [6,8,9].

HREEL vibrational spectra for the three ordered structures on Rh(111) at 300 K are similar to those of benzene plus CO adsorbed on Pt(111) in Fig. 1. However, only one C-O stretching mode is observed for the ordered

CO/benzene structures on Rh(111) instead of the two modes seen for the ordered structures on Pt(111). The C-O stretching frequency is 1655 cm^{-1} for CO adsorbed within a $c(2\sqrt{3}\times 4)\text{rect}$ unit cell and 1700 cm^{-1} within (3×3) unit cell. There is only one way to mutually arrange one benzene molecule and the correct number of CO molecules within a $c(2\sqrt{3}\times 4)\text{rect}$ unit cell or a (3×3) unit cell. These arrangements are shown in Figs. 2C and D. The CO molecules are assumed to be chemisorbed in hollow sites because the low C-O stretching frequency is in the range observed for CO bonded to three metal atoms in metal-carbonyl clusters [10]. A dynamical LEED analysis for the $c(\sqrt{3}\times 4)\text{rect}$ structure has been reported previously [8] where the authors assumed no CO molecule was present within the unit cell. The same authors have recently repeated this analysis including coadsorbed CO within the unit cell. This analysis confirms the geometry proposed in Fig. 2C for the $c(2\sqrt{3}\times 4)\text{rect}$ structure and will be discussed in detail in a future publication.

While the chemisorption of CO in three-fold hollow sites on metal surfaces has been suggested to occur in certain cases [11], the experimental results we report here provide strong evidence for the bonding of a CO molecule at a hollow-site on a metal surface. As shown in Fig. 2, those CO molecules nearest to adsorbed benzene molecules bond at hollow sites for all ordered structures observed on Pt(111) and Rh(111). The C-O stretching frequency for CO bonded in the hollow sites provides information about the interaction between coadsorbed CO and benzene since this frequency is substantially lower than those observed for CO adsorbed on platinum and rhodium surfaces without coadsorbed benzene. Low C-O stretching frequencies have also been observed for CO coadsorbed with alkali atoms on metal surfaces [12] where the reduction is caused by charge donation

from the alkali atoms through the substrate and into the $2\pi^*_{CO}$ orbital [13]. Our data indicate a similar effect occurs when CO is coadsorbed with benzene. The presence of ordered structures that contain both CO and benzene intermixed in the same unit cell and the persistence of ordered structures at CO and benzene coverages away from stoichiometric concentrations further indicate an attractive interaction exists between coadsorbed CO and benzene.

The attractive interaction between coadsorbed CO and benzene along with the repulsive dipole-dipole interaction between CO molecules is responsible for CO-induced ordering of benzene on Pt(111) and Rh(111). These interactions result in the potential energy contribution to the surface free energy being minimized when CO and benzene form an ordered monolayer where adsorbed molecules have the maximum number of unlike nearest neighbors and where adsorbed CO molecules are separated by the greatest distance possible. This effect is well known in the thermodynamics of solid solutions where interactions between substituents stabilize an ordered phase [14]. As shown in Fig. 2, coadsorbed CO and benzene do order in this manner except for the $(2\sqrt{3}\times 4)$ rect structure on Pt(111). In this structure, the benzene and CO molecules form a zig-zag arrangement along the Pt(111) surface probably due to an attractive benzene-benzene interaction competing with the CO-benzene interaction.

In summary, 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, any adsorbed molecule which has an attractive interaction with adsorbed carbon monoxide and has enough mobility on the surface should form an ordered overlayer upon the addition of CO. 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.

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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. Van der Waals dimensions are shown.

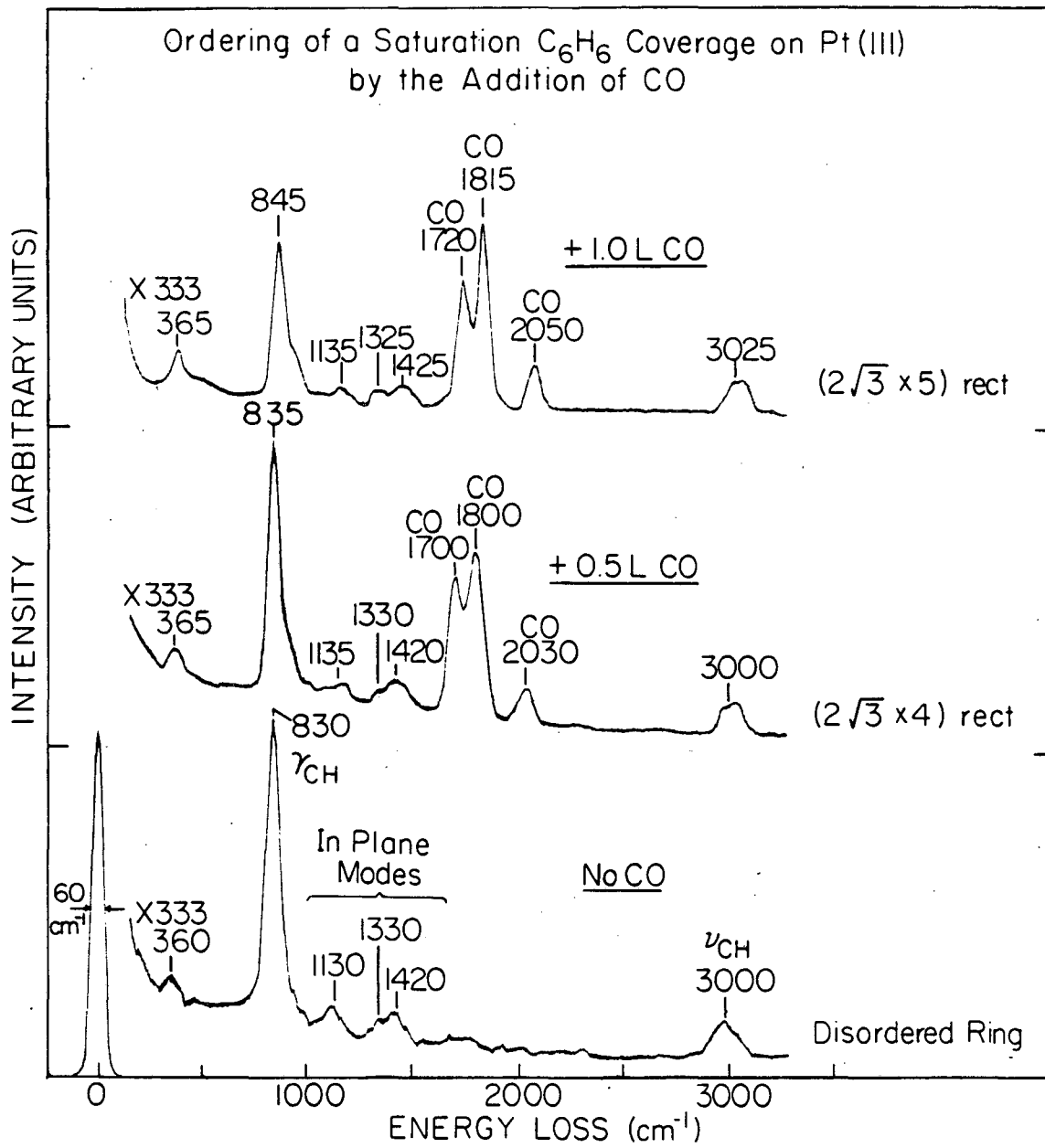
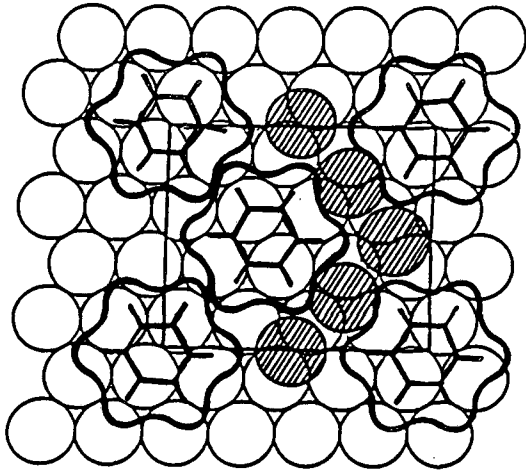
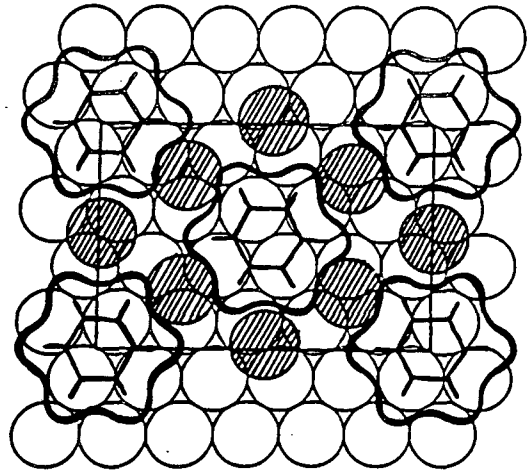
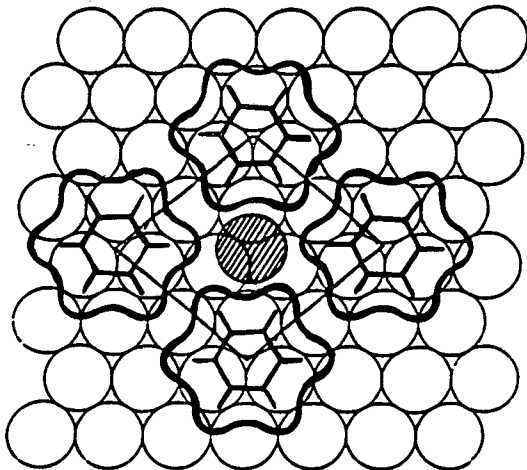
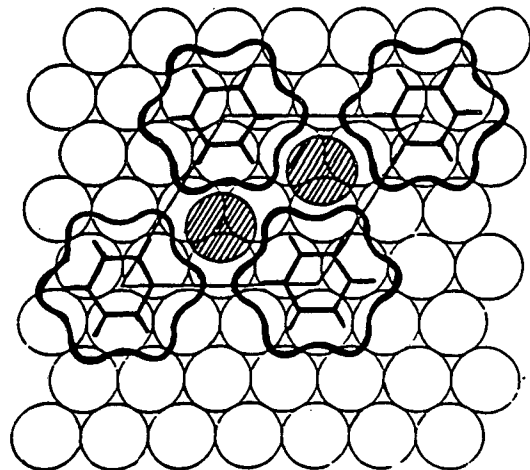


Fig. 1

$$\text{CO/C}_6\text{H}_6/\text{Pt (III)}$$
(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) (3×3) 

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Fig. 2

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