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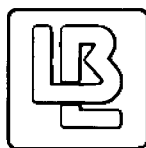
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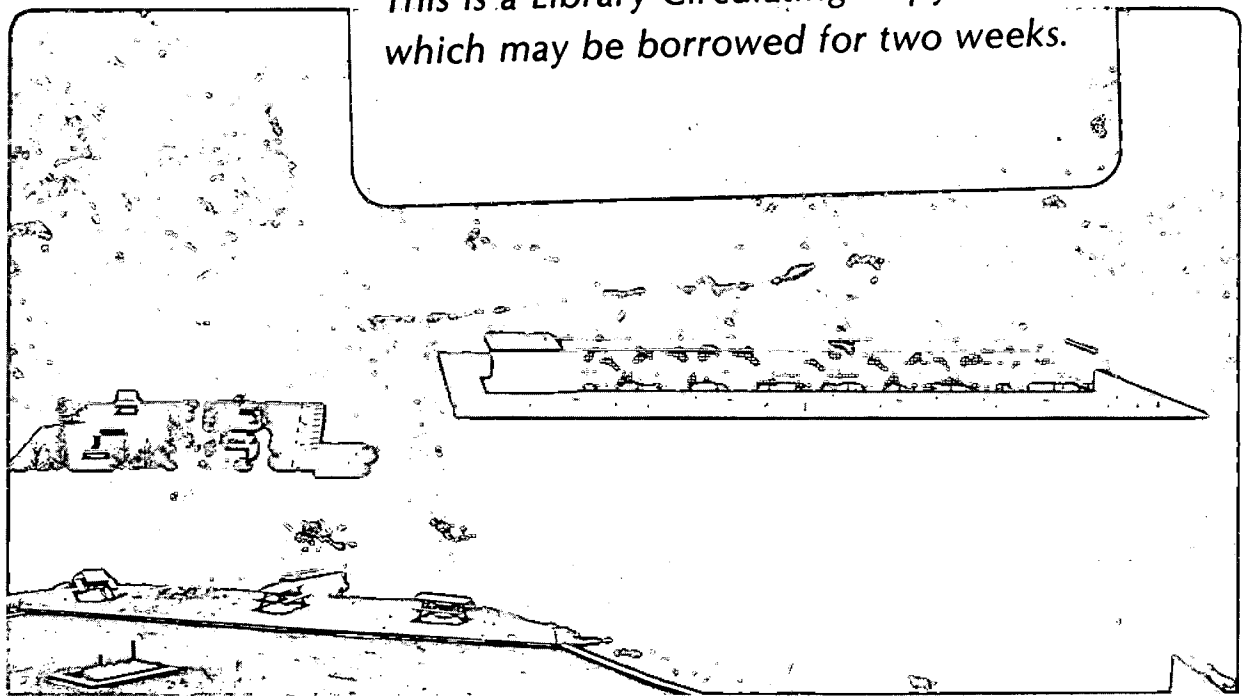
THE STRUCTURES OF CO, NO AND BENZENE ON VARIOUS TRANSITION METAL SURFACES: OVERVIEW OF LEED AND HREELS RESULTS

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The Structures of CO, NO and Benzene on Various Transition Metal Surfaces: Overview of LEED and HREELS Results

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Recent results are summarized concerning the adsorption structures of carbon monoxide (CO) and nitric oxide (NO) chemisorbed on various transition metal surfaces, and of benzene (C₆H₆) on Pd, Rh and Pt(111). These results were for the most part obtained with intensity analysis of low-energy electron diffraction (LEED) and high-resolution electron energy loss spectroscopy (HREELS).

1. Introduction

A substantial collection of adsorption geometries is now known for CO, NO and benzene adsorbed on transition metal surfaces. The available structural information includes adsorption sites, molecular orientation, bond lengths and bond angles. These structures provide insight into the adsorption mechanism, especially when cases of coadsorption are considered. When supplemented with thermal desorption spectroscopy and work function measurements, a comprehensive picture emerges, which includes a sizable electronic charge transfer between adsorbates through the metal substrate.

The experimental and theoretical techniques employed in LEED and HREELS can be found described in references [1] and [2], respectively. LEED provides bond length and bond angle information, while HREELS identifies adsorbed molecular species and indicates their orientation.

2. CO and NO Structures

Table 1 details all CO and NO adsorption structures determined on single-crystal surfaces by electron diffraction methods. The result on Ni(111) was obtained with angle-resolved normal photoelectron diffraction [7]. In addition, structural data for metal carbonyl complexes are summarized for comparison [16]. CO and NO behave very similarly in these structural studies.

The adsorption sites for CO and NO found with LEED correspond closely with those predicted from the vibrational assignment based on the metal carbonyl results [2,18]. This includes the case of coadsorption of CO or NO with hydrocarbons (benzene and ethylidyne, C₂H₃). The most recent result is that of CO on Pd(111), which at a 1/3 monolayer coverage adsorbs over a three-fold hollow site, a rare choice for pure CO on metal surfaces. In all cases the CO and NO molecular axes are found to be perpendicular to the surface. In two very compact (2x2) structures of CO and NO on Rh(111), some of the molecules adsorb in low-symmetry sites slightly away from top sites, such that tilting from the surface normal is conceivable. LEED indicates that any tilting would be less than approximately 5° in those cases.

Table 1. Adsorption geometries of carbon monoxide and nitric oxide, indicating metal-carbon, metal-nitrogen, C-O and N-O bond lengths, as well as adsorption sites on various metal substrates

System	$d_{M-C,N}(\text{\AA})$	$d_{C,N-O}(\text{\AA})$	site
Pure CO/Surface			
Pt(111)-c(4x2) - 2CO ³	1.85 ± 0.1	1.15 ± 0.05	top
	2.08 ± 0.07	1.15 ± 0.05	bridge
Rh(111)-($\sqrt{3} \times \sqrt{3}$)R30° - CO ⁴	1.95 ± 0.1	1.07 ± 0.1	top
Rh(111)-(2 × 2) - 3CO ⁵	1.94 ± 0.1	1.15 ± 0.1	top
	2.03 ± 0.07	1.15 ± 0.1	bridge
Pd(111)-($\sqrt{3} \times \sqrt{3}$)R30° - CO ⁶	2.05 ± 0.04	1.15 ± 0.05	fcc hollow
Ni(111)-($\sqrt{3} \times \sqrt{3}$)R30° - CO ⁷	1.78 ± 0.04	1.13 ± 0.05	bridge
Ni(100)-c(2 × 2) - CO ⁸	1.75 ± 0.1	1.15 ± 0.1	top
Cu(100)-c(2 × 2) - CO ⁸	1.90 ± 0.1	1.13 ± 0.1	top
Pd(100)-(2 $\sqrt{2} \times \sqrt{2}$)R45° - 2CO ⁹	1.93 ± 0.07	1.15 ± 0.1	bridge
Ru(0001)-($\sqrt{3} \times \sqrt{3}$)R30° - CO ¹⁰	2.00 ± 0.07	1.10 ± 0.1	top
Coadsorbed CO			
Rh(111)-c(4x2) - CO + C ₂ H ₃ ¹¹	2.02 ± 0.04	1.17 ± 0.05	hcp hollow
Pd(111)-(3 × 3) - 2CO + C ₆ H ₆ ¹²	2.05 ± 0.04	1.17 ± 0.05	fcc hollow
Rh(111)-c(2 $\sqrt{3} \times 4$)rect - CO + C ₆ H ₆ ¹³	2.16 ± 0.04	1.21 ± 0.05	hcp hollow
Rh(111)-(3 × 3) - 2CO + C ₆ H ₆ ¹⁴	2.02 ± 0.07	1.17 ± 0.1	hcp hollow
Pt(111)-(2 $\sqrt{3} \times 4$)rect - 4CO + 2C ₆ H ₆ ¹⁵	1.99 ± 0.07	1.15 ± 0.1	bridge
Metal carbonyl complexes			
CO on metal clusters ¹⁶	2.00 - 2.23	1.15 - 1.21	hollow
CO on metal clusters ¹⁶	1.82 - 2.09	1.07 - 1.18	bridge
CO on metal clusters ¹⁶	1.70 - 1.91	1.01 - 1.18	top
Pure NO/Surface			
Rh(111)-(2x2) - 3NO ¹⁷	1.94 ± 0.1	1.15 ± 0.1	near-top
	2.05 ± 0.07	1.15 ± 0.1	bridge
Coadsorbed NO			
Rh(111)-c(4x2) - NO + C ₂ H ₃ ¹¹	2.02 ± 0.04	1.17 ± 0.05	fcc hollow

There are two different 3-fold coordinated hollow sites at fcc(111) surfaces. They are distinguished by the presence (hcp hollow) or absence (fcc hollow) of metal atoms directly below in the second metal layer. It is found that CO on Rh(111) systematically prefers the hcp over the fcc hollow site, while CO on Pd(111) prefers the fcc over the hcp hollow site.

There is a preference for higher-coordination sites for CO and NO when coadsorbed with hydrocarbons. The same effect is well known from vibrational measurements for CO coadsorbed with alkali atoms. This implies significant charge transfer from the hydrocarbon species to the CO and NO. Such charge transfer is confirmed by work function measurements, which also indicate that these hydrocarbon species are electron donors.

The metal-carbon and metal-nitrogen bond lengths show a strong dependence on the site coordination. These bond lengths increase from about 1.8-1.9Å on top sites, via about 1.8-2.0Å on bridge sites to about 2.0-2.1Å on hollow sites. The C-O and N-O bond lengths vary rather less, but exhibit a trend toward elongation with coadsorption of electron donors. Thermal desorption spectroscopy indicates a strengthening of the metal-carbon bonds with such coadsorption, while large decreases in C-O and N-O stretch frequencies are observed, showing intra-molecular weakening. This is a further example of coadsorbate-induced tendency toward CO and NO decomposition, as is familiar from alkali coadsorption.

3. Benzene Structures

Table 2 collects the structures of adsorbed benzene as determined to date by LEED and HREELS. They are all coadsorption structures with CO, because benzene alone does not order well on these metal surfaces.

Benzene has been found to remain molecularly adsorbed parallel to the surface up to saturation coverage and up to the decomposition temperature (450-550K, depending on the metal). Centering of the benzene ring on hollow sites is favored on Rh and Pd, while bridge-centering occurs on Pt, at least when coadsorbed with CO.

The latest structure is illustrated in Fig. 1. It concerns benzene coadsorbed with CO on Pd(111), with a 1:2 ratio of the two kinds of molecules. It has the same (3x3) unit cell as an earlier very similar structure analyzed on Rh(111). The molecular arrangement is nearly indistinguishable, except for a shift from one type of hollow site to the other.

However, a significant difference with respect to the three earlier benzene structures has emerged: the C₆ ring distortion observed on the other metals is not detected on Pd(111). The distortion on Rh and Pt(111) involves primarily a large expansion of the C₆ ring radius, with in addition alternations among the C-C bond lengths (see Table 2). A trend toward more distortion can be seen in going from Pd via Rh to Pt, while the metal-carbon bond lengths decrease in that sequence. This is consistent with thermal desorption results that indicate a simultaneous strengthening of the metal-carbon bond and a tendency to easier decomposition.

Some of the benzene structures discussed above have been examined with other structural techniques as well, with somewhat different conclusions. From angle-resolved photoemission data, benzene on Rh(111), with or without coadsorbed CO, is concluded to exhibit a 6-fold symmetry [20]. This would exclude alternating C-C distances, but not a ring expansion. With near-edge x-ray absorption fine structure, benzene on Pt(111) was studied in the absence of coadsorbed CO [21]. The C-C bond lengths were estimated to be indistinguishable from the gas-phase values. On the other hand, as Table 2 shows, x-ray diffraction results from benzene in organometallic complexes do detect a ring expansion and C-C bond length alternations [19]. These possible discrepancies remain to be explained.

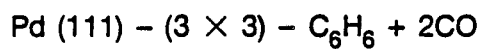
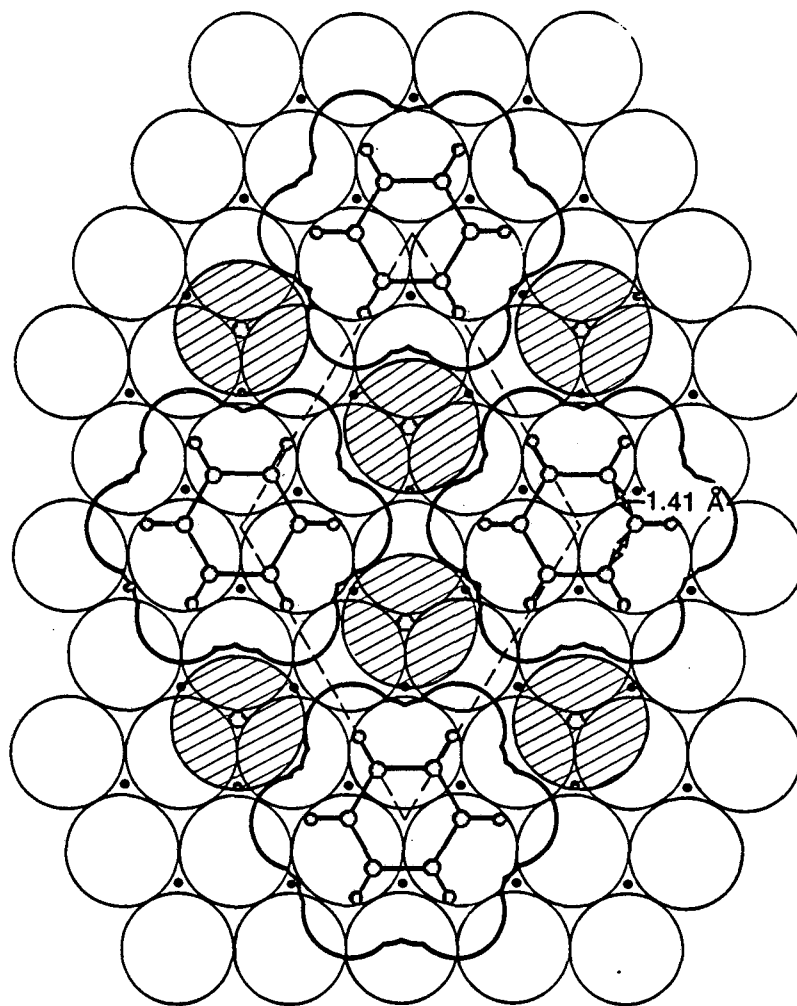
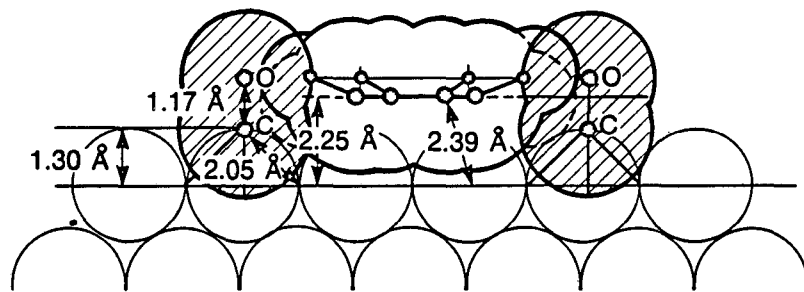
Table 2. Adsorption geometries of benzene, indicating average carbon-ring radius, C-C bond lengths (two values where long and short bonds coexist), metal-carbon distances and adsorption sites of C₆H₆ ring centers

System	C ₆ radius	$d_{C-C}^{\text{avg}}(\text{Å})$	$d_{M-C}(\text{Å})$	site
benzene/surface				
Pd(111) - (3 × 3) - C ₆ H ₆ + 2CO ¹²	1.41 ± 0.10	1.41 ± 0.10	2.39 ± 0.05	fcc hollow
Rh(111) - (3 × 3) - C ₆ H ₆ + 2CO ¹⁴	1.51 ± 0.15	1.58 ± 0.15 1.46 ± 0.15	2.30 ± 0.05	hcp hollow
Rh(111) - c(2√3 × 4)rect - C ₆ H ₆ + CO ¹³	1.65 ± 0.15	1.81 ± 0.15 1.33 ± 0.15	2.35 ± 0.05	hcp hollow
Pt(111) - (2√3 × 4)rect - 2C ₆ H ₆ + 4CO ¹⁵	1.72 ± 0.15	1.76 ± 0.15 1.65 ± 0.15	2.25 ± 0.05	bridge
benzene/complex				
C ₆ H ₆ on Ru ₆ , Os ₃ clusters ¹⁹	1.44	1.48 1.39	2.27 - 2.32	hollow
gas				
C ₆ H ₆ molecule	1.397	1.397		
C ₂ H ₆ molecule		1.54		
C ₂ H ₄ molecule		1.33		
C ₂ H ₂ molecule		1.20		

4. Conclusions

The structural results summarized here exhibit details of reaction pathways followed by CO and benzene over transition metal surfaces, through clear correlations that are seen between structural variations and reaction mechanisms. A significant contribution is found from charge transfer between coadsorbates and perhaps between the adsorbates and the substrates.

It is also found that coadsorbates of opposite donor/acceptor character mix well on single-crystal metal surfaces. These mixed overlayers are characterized by attractive interactions between donors and acceptors and by a greater stability against thermal disorder than for the pure adsorbate layers. A result is cooperatively ordered overlayers.



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Figure 1. Side view and top view of benzene coadsorbed with CO on Pd(111). Van der Waals radii are assumed for overlayer atoms. Large dots indicate C and O positions, medium dots indicate guessed hydrogen positions, and small dots represent metal atoms in the second metal layer. The CO molecules are shaded. A (3x3) unit cell is outlined

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