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LOW ENERGY ELECTRON DIFFRACTION AND WORK
FUNCTION STUDIES OF BENZENE, NAPHTHALENE AND
PYRIDINE ABSORBED ON Pt(111) AND
Pt(100) SINGLE CRYSTAL SURFACES

J. L. Gland and G. A. Somorjai

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Low Energy Electron Diffraction and Work Function Studies
of Benzene, Naphthalene and Pyridine Adsorbed on
Pt(111) and Pt(100) Single Crystal Surfaces

J. L. Gland and G. A. Somorjai

Inorganic Materials Research Division, Lawrence Berkeley Laboratory,
and Department of Chemistry; University of California
Berkeley, California 94720

Abstract

Benzene, naphthalene, and pyridine adsorb readily on the Pt(111) and Pt(100)-(5×1) surfaces. Adsorption of these aromatic molecules leads to the formation of ordered structures on the Pt(111) surface while adsorption on the Pt(100) surface leads to the formation of poorly ordered surface layers. Benzene adsorbed on the Pt(111) surface at 25°C causes the formation of the Pt(111)- $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 4\hat{a} & 4\hat{b} \end{vmatrix}$ -Benzene structure with a corresponding work function change of approximately -1.4 V. With further benzene exposure the initial ordered structure is transformed to the Pt(111)- $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 5\hat{a} & 5\hat{b} \end{vmatrix}$ -Benzene structure with a work function change of approximately -0.7 V. This transformation is the result of a reorientation of the adsorbed benzene molecules. Naphthalene forms the Pt(111)-(6×6)-Naphthalene structure when adsorbed on the Pt(111) surface at 150°C and the work function change on adsorption is about -2.0 V. Pyridine forms two poorly ordered structures on the Pt(111) surface. The large work function change on adsorption of pyridine (-2.5 V) indicates that the nitrogen participates in the adsorbate-substrate bond.

Introduction

The predominance of ordered adsorption on low index single crystal surfaces has been one of the significant findings resulting from Low Energy Electron Diffraction studies. Many of the molecules commonly used as adsorbates to date were small, with molecular dimensions less than the interatomic distances in the substrate.¹ The adsorbed molecules can form structures with the rotational symmetry of the substrate such that the unit vectors of the surface structure are closely related to the substrate unit vectors.² For large molecules whose dimensions are many times larger than the substrate interatomic distance, ordering on surfaces may depend on the substrate characteristics in a more complex manner. These molecules may interact simultaneously with a large number of surface atoms, so the structures they form may be less restricted by the periodicity of the substrate. For example, xenon forms an ordered xenon crystal with (111) orientation regardless of substrate rotational symmetry when adsorbed on several surfaces.³ In this case, we see a predominance of the adsorbate-adsorbate interaction in determining the surface structure since the adsorbate-substrate interaction potential is fairly uniform across the surface.

In order to characterize adsorbed layers of large molecules, we have investigated the adsorption of benzene, naphthalene, and pyridine on Pt(111) and Pt(100)-(5x1) surfaces in the temperature range 25°C to 300°C. These studies utilized Low Energy Electron Diffraction (LEED) and work function change (WFC, $\Delta\phi$) as experimental probes of the adsorbed

layer. The LEED patterns and the corresponding WFC were monitored as a function of incident flux, exposure time, and surface temperature.

Ordering and WFC were both dependent on the magnitude of the incident flux, the exposure time, the temperature, and substrate structure. Benzene formed ordered structures on the Pt(111) surface. The adsorbed layer of benzene undergoes a transformation from the Pt(111)- $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 4\hat{a} & 4\hat{b} \end{vmatrix}$ Benzene structure to the Pt(111)- $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 5\hat{a} & 5\hat{b} \end{vmatrix}$ Benzene structure. Naphthalene forms a (6x6) structure on the Pt(111) surface. Pyridine adsorbed on the Pt(111) surface at 25°C produces a poorly ordered structure with a characteristic distance twice the size of the substrate unit cell. At higher temperatures (250°C) pyridine forms a fairly ordered one dimensional structure with the characteristic dimension three times the distance in the underlying lattice. Benzene adsorption on the Pt(100)-(5x1) surface produced a poorly ordered structure with a characteristic distance twice that of the substrate, while naphthalene on the Pt(100) surface remained disordered. Pyridine forms a disordered layer at room temperature on the (100) surface; however, at 250°C it forms a very poorly ordered ($\sqrt{2}\times\sqrt{2}$)R-45° structure. Recent studies of benzene adsorption on the Ni(110) and Ni(111) surfaces have also shown exposure dependent behavior for benzene on these surfaces.⁴ These studies, when extended to benzene and naphthalene derivatives and to other substrate surfaces, may yield detailed information concerning the nature of the substrate adsorbate interactions and the relationship of these interactions to the process of ordering of large adsorbed molecules on solid surfaces.

Experimental

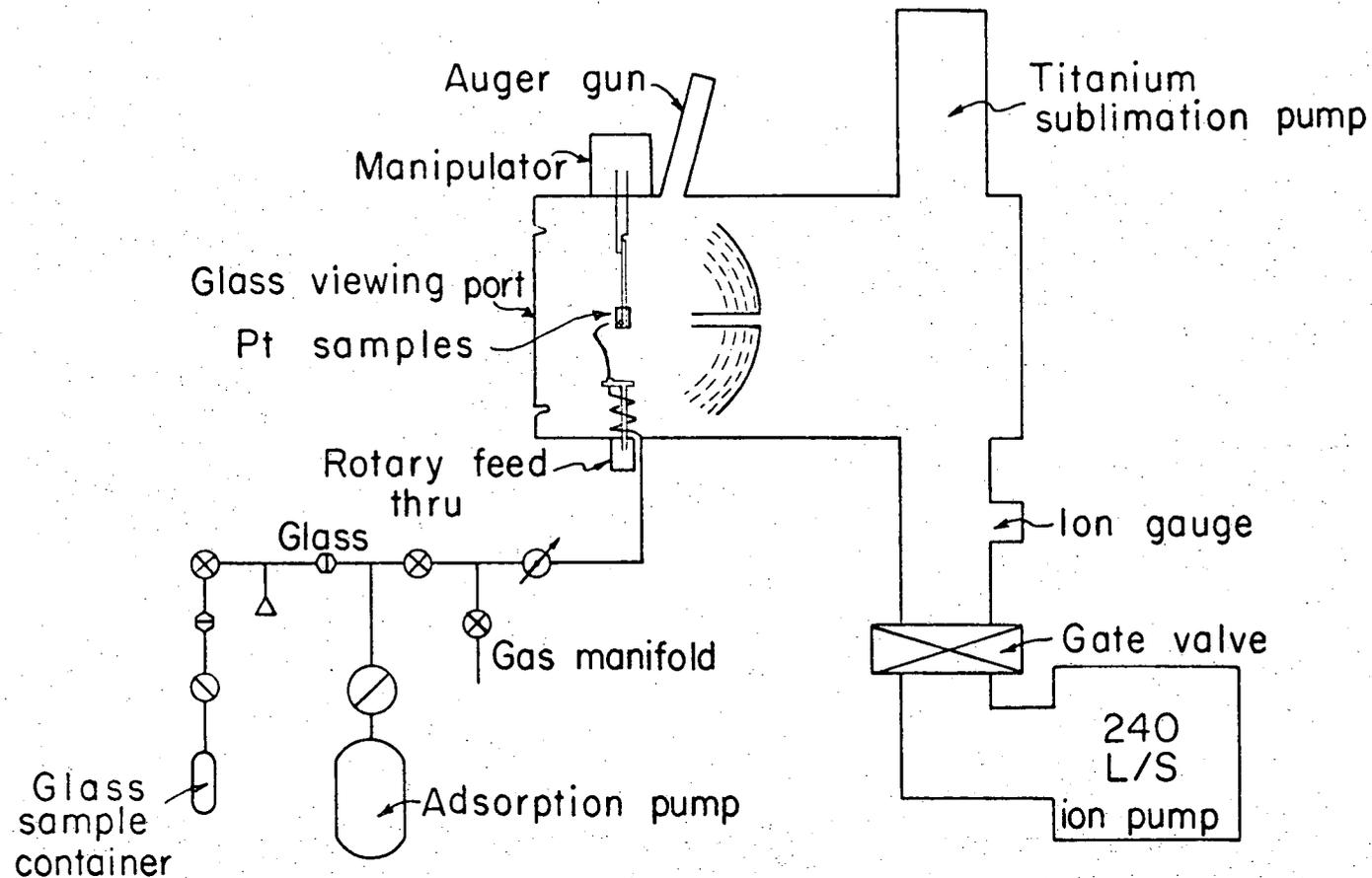
A modified Varian LEED apparatus has been used in these studies. It is equipped with a 240 liter/second Vacion pump, a water cooled titanium sublimation pump and an auxiliary 8 liter/sec Vacion pump. Typical ambient pressure for the system is 2×10^{-9} torr during periods of daily use.

The platinum single crystals used in these studies were electron beam zone refined samples purchased from Materials Research Corporation. They were aligned ($\pm .5^\circ$) using Laue back reflection technique, and spark cut and polished with a series of abrasives. The final polish was with 0.5μ Al_2O_3 powder. They were etched for 30 minutes in 1:1 diluted aqua regia at 100°C immediately prior to insertion into the vacuum system. The samples are discs 6 millimeters in diameter with a thickness of .85 mm. The samples were spot welded to polycrystalline platinum holders (99.99% pure), 1 mm thick, 3 mm wide and 5 mm long. These platinum holders were supported by two tantalum bars 6 mm by 6 mm in cross section. Heavy holders were used so that the position of the sample would be constant with repeated heating and cooling and so that the samples would be the hottest part of the system. Two samples were mounted back to back on separate polycrystalline holders. Thus LEED observations could be made and work function measurements taken for both samples under identical experimental conditions by simply rotating the sample by 180° . Heating and cooling were carried out simultaneously on both crystal faces. Direct current resistance

heating has been used. At a temperature of 1000°C (approximately 120 amps heating current) the crystals had a 5° temperature gradients across their surfaces while the two sample surfaces were within 20° of each other (temperatures taken with a calibrated optical pyrometer). Temperatures quoted were measured with a platinum/platinum-10% rhodium thermocouple spot welded to the top edge of the Pt(100) sample.

A rotatable capillary tube was used to introduce all gases directly onto the crystal surface from a distance of 5 mm. Oxygen used for cleaning was research grade O₂ (99.99%) used without further purification. The vapor pressures of the organic molecules studied were high enough to permit the use of a simple glass inlet system with Teflon valves. A schematic of the system used is shown in Figure 1.

Cleaning was routinely carried out before each experiment. The crystals were heated to 1000°C and O₂ flowed over them at pressures of 1 to 3×10⁻⁵ torr for 30 minutes on each side. The auxiliary 8 liter/sec ion pump was used for pumping the oxygen. After terminating the O₂ flow, the system was pumped down to a pressure of 1×10⁻⁸ torr using the large ion pump and the sublimation pump. The electron guns were then degassed and the crystals and chamber (hot from radiant heating) were allowed to cool. Measurement of the work function change made a 5 hour stabilization period for the LEED gun necessary. Following gun stabilization the crystals were heated to 1000°C for 5 minutes. The surface produced in this manner was clean within the limits detectable by Auger electron spectroscopy and showed the characteristic Pt(111)-(1×1) and Pt(100)-(5×1) diffraction patterns. The crystal was allowed to cool to 25°C in a background



-5-

- △ Thermocouple gauge
- ⊗ Valve
- ⊘ Variable leak valve
- ⊙ Coupling

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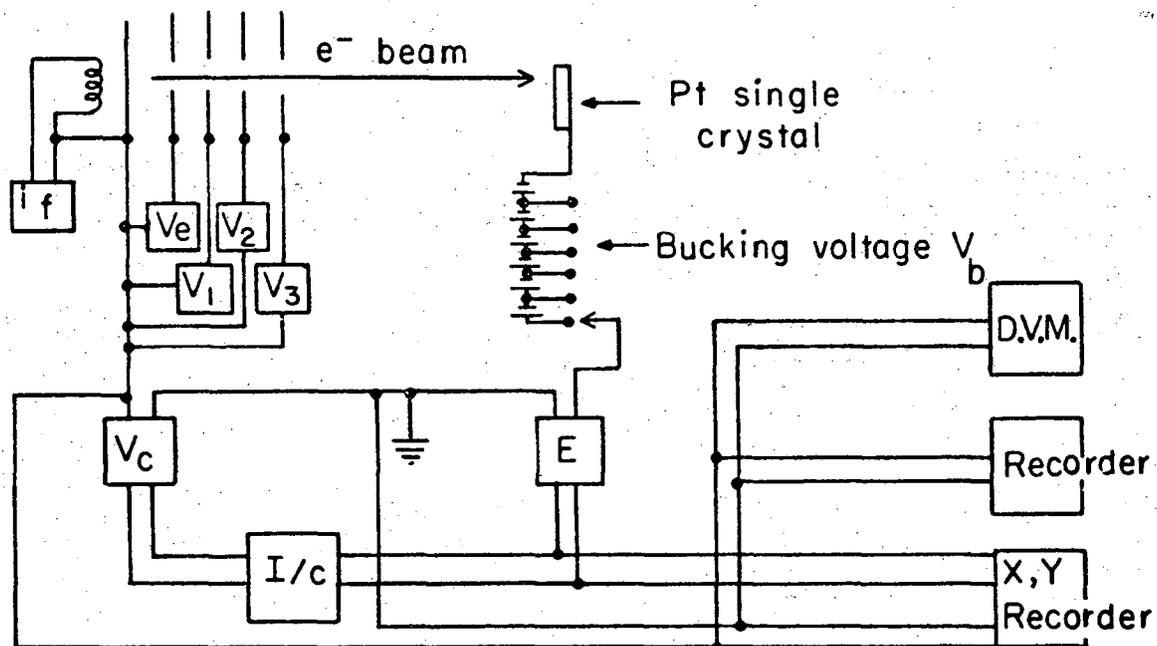
Figure 1 A schematic diagram of the ultra-high vacuum system used in the adsorption studies.

pressure of 1×10^{-9} torr. The organic vapor was then introduced at the desired pressure. Fluxes at the crystal surface can only be approximated since the ion gauge used to record pressure was in the mouth of the ion pump far from the crystal surface. The effective pressure P at the surface can be calculated from the recorded pressure, p , by the equation⁵

$$P(\text{torr}) = \frac{pT}{39 + 7.08(T/M)^{1/2}}$$

for our experimental geometry and pumping speed. This equation was derived assuming isotropic hemispherical effusion from a point source.⁵ M is the molecular weight of the gas being considered; T is the temperature in $^{\circ}\text{K}$; and the constants reflect the geometry of the system. At 300°K this equation becomes $P = \frac{p}{.13 + .41(M)^{-1/2}}$. For benzene and pyridine at this temperature the equation becomes $P \approx 5.7p$; for naphthalene $P \approx 6p$. These equations are approximate and hold only for the case in which molecular flow predominates. During the course of the experiments (several hours) each surface was exposed to the incident flux approximately for the same time period. The condition of the surface which was not being exposed at the time was monitored alternately by LEED and work function measurements.

The work function change has been measured using a variation of the retarding field method as outlined by Chang.⁶ A schematic of the equipment is shown in Figure 2. The work function reference was obtained before adsorption by recording a group of current (i_c) versus voltage (V_c) curves for a series of bucking voltages (V_b). The same measurement is made after adsorption; thus the difference between the current vs. voltage curves (before and after adsorption) for a given bucking voltage is the uncorrected work function change $\Delta\phi'$. Since



- | | | | |
|-------|---------------------------------------|-------|---------------------|
| E | Electrometer (current to the crystal) | V_2 | Second grid supply |
| V_c | Cathode voltage supply | V_3 | Third grid supply |
| i_f | Filament current supply | I/c | Inverter/comparator |
| V_e | Extractor voltage supply | DVM | Digital voltmeter |
| V_1 | First grid supply | | |

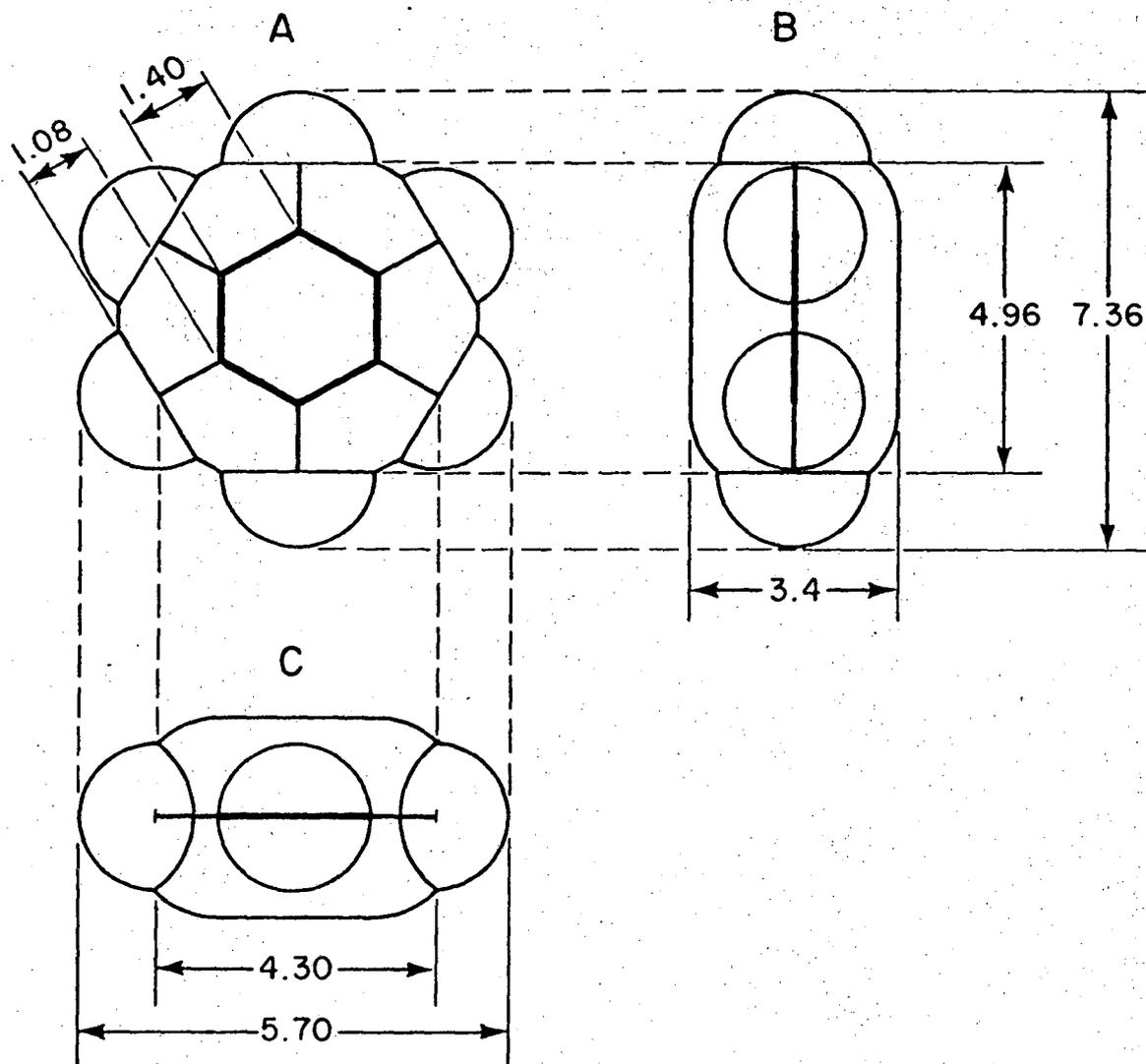
Figure 2 A schematic diagram of the system used for work function change measurements.

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the bucking voltage changes are known, they are used as an internal standard to correct for any deviations from unity gain. The gain of the system has been defined as $\frac{\Delta V_b \text{ experimental}}{\Delta V_b \text{ actual}}$. That is, the voltages between the V_c vs. i_c curves are taken (ΔV_b experimental) at a given current (i_c) for a series of bucking voltages (V_b). Then bucking voltages are measured with a calibrated digital voltmeter. The ratio between ΔV_b (exp) and ΔV_b is the gain of the system. The crystal was positioned so that any spurious contribution to the work function change from the polycrystalline holder or edges of the crystal would be minimized. However, a gain of unity could not be achieved in this configuration as was the case in the studies by Chang.⁶ The gain depends on the shape of the beam and the position of the beam on the crystal. A gain of one could not be achieved with the optimum crystal position since the beam was focused on the lower part of the crystal and was deflected downward with increasing bucking voltage. The gain is a characteristic of the system geometry and thus remains constant during adsorption. In fact the gain remains constant (within $\pm 1\%$) even though the external magnetic field is not compensated for and the filament temperature is not known precisely. All values of the detected work function changes reported here have been divided by the gain: for Pt(111), gain = 1.027, for Pt(100), gain = 1.075. The Varian LEED gun was used for the WFC measurements but the voltages on the gun elements and the filament heating current are supplied by auxiliary regulated power supplies stable to .1% over several days. The current measurements were taken using a Keithley Electrometer

Model 610B. Data has been collected at bucking voltages of -1.353 volts to -8.118 volts since the gain was constant over this voltage range and the V_c versus i_c curves were parallel for the above bucking voltages over the current range -2×10^{-8} amps to -1.0×10^{-7} amps. The cathode voltages used ranged from -7 volts to -25 volts. Data were taken using several techniques: (1) by plotting the cathode voltage (V_c) versus current to the crystal (i_c) curves for a series of bucking voltages using an X,Y recorder; (2) by recording the voltage V_c required to achieve a given current using a digital voltmeter for voltage measurements; (3) by using a time base recorder to record V_c and an automatic system for controlling V_c so that the current to the crystal was constant. This last method allows a continuous monitoring of work function during adsorption and subsequent exposure. The automatic system uses an inverter comparator on the recorder output of the electrometer to control the cathode voltage so that a constant current is incident on the crystal (at fixed bucking voltage). The slope of the V_c vs. i_c curves is effected by changes in the secondary emission characteristics of the surface; no such effects have been observed during these adsorption studies. The homogeneity of the surface can be estimated by comparing the WFC recorded at different bucking voltages since the beam moves along the crystal surface as the bucking voltage is changed. In these studies this effect has been seen on surfaces shown to be inhomogeneous by LEED.

The molecular dimensions of benzene, naphthalene and pyridine are shown in Figures 3, 4 and 5, respectively. The interatomic distances

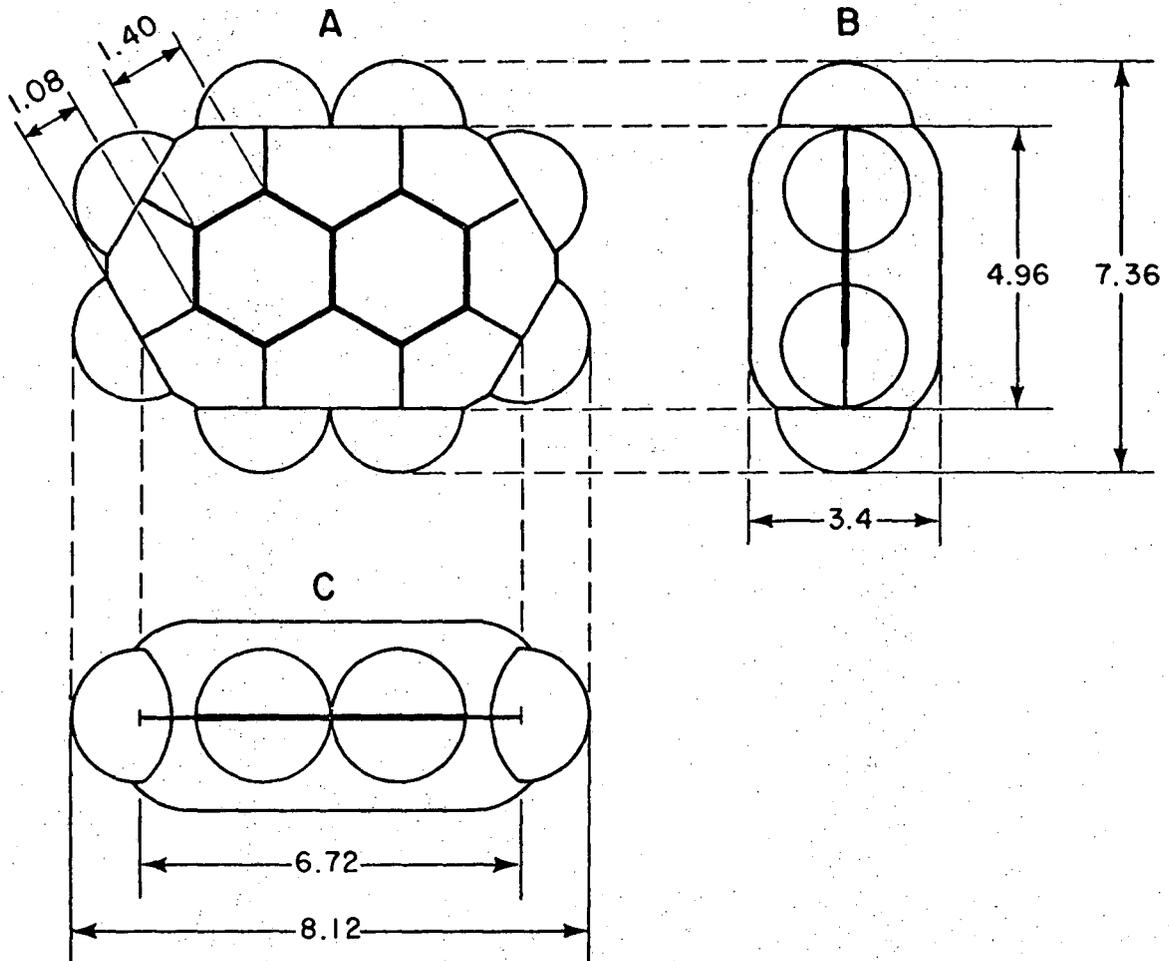


Benzene

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Figure 3 The structure of benzene with van der Waals radii shown.

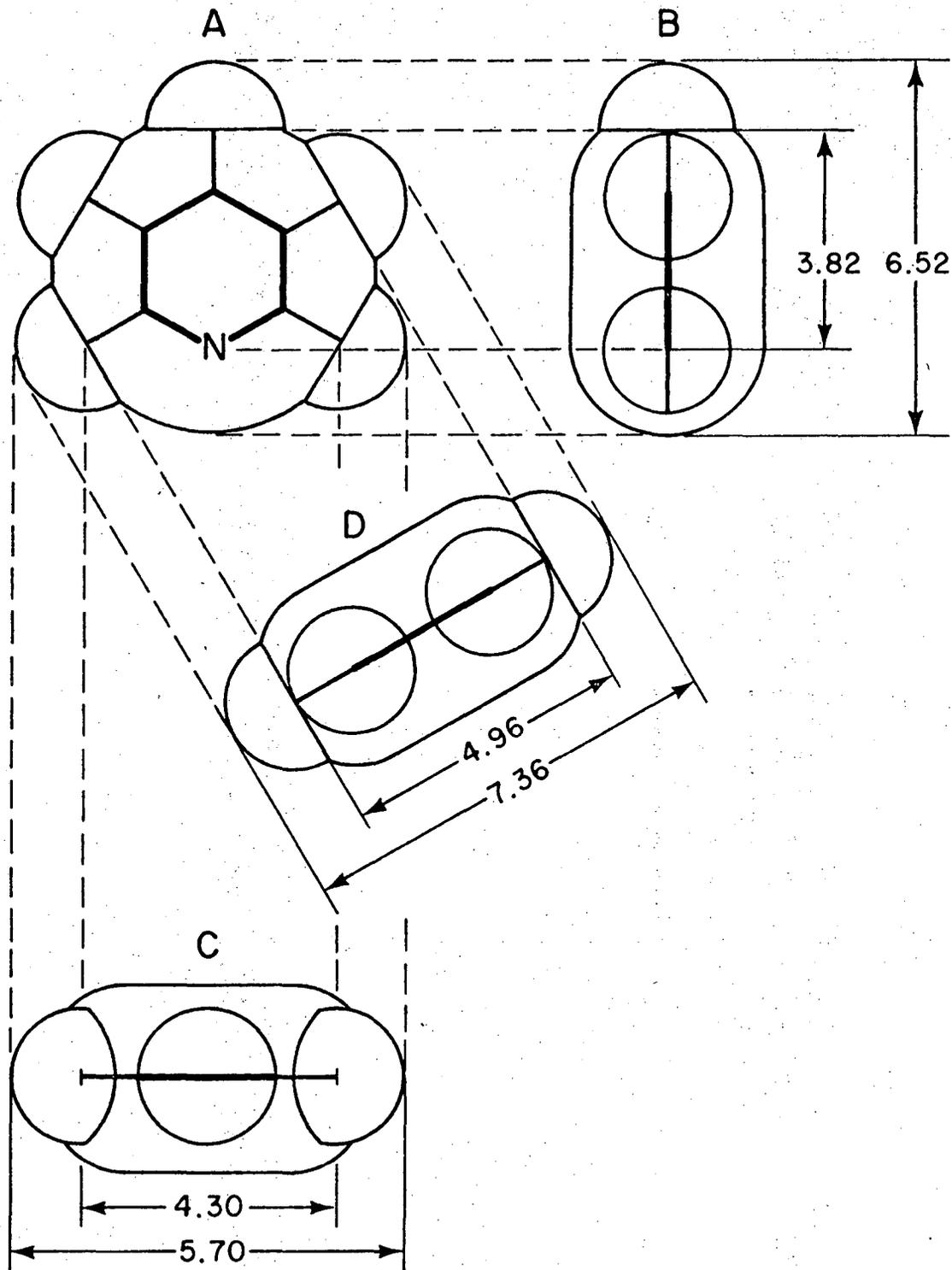
All dimensions are in angstroms.



Naphthalene

XBL 7211-7289

Figure 4 The structure of naphthalene with van der Waals radii shown.
All dimensions are in angstroms.



Pyridine

XBL 7211-7285

Figure 5 The structure of pyridine with van der Waals radii shown. The C-C distance (1.40 \AA) and the C-H distance (1.08 \AA) are not shown since they are the same as benzene.

and geometry⁷ are given to the closest .1 Å. The van der Waals radius used for hydrogen is 1.2 Å.⁸ The thickness used for the aromatic system is 3.4 Å.⁸ The molecules are shown in various projections since the experiments (discussed below) indicate that the molecules undergo a change in orientation while adsorbed on the platinum surface. The vapor pressures at 25°C are 104.3 torr for benzene, 7×10^{-2} torr for naphthalene, and 20.5 torr for pyridine.⁹ The enthalpies of vaporization of benzene and pyridine (7.353 kcal/mole and 8.392 kcal/mole¹⁰) indicate that multilayer adsorption is not likely considering our experimental conditions ($T > 273^\circ\text{K}$, the effective pressure $P < 10^{-5}$ torr). For naphthalene the enthalpy of sublimation 17.7 kcal/mole¹⁰ indicates that multilayer adsorption is not probable with our experimental conditions.

Results

Benzene, naphthalene and pyridine adsorb on both the Pt(111) and Pt(100)-(5×1) surfaces, forming structures which exhibit much better order on the Pt(111) surface than on the Pt(100)-(5×1) surface.

Benzene adsorption: Benzene adsorbed on the Pt(111) surface initially forms a poorly ordered layer. Continued exposure causes the appearance of the Pt(111) - $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 4\hat{a} & 4\hat{b} \end{vmatrix}$ -Benzene structure (Fig. 6A).¹¹ With continued exposure this structure changes to the Pt(111)- $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 5\hat{a} & 5\hat{b} \end{vmatrix}$ -Benzene structure (Figs. 6A, 7A,B,C). The transformation from the $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 4\hat{a} & 4\hat{b} \end{vmatrix}$ structure to the $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 5\hat{a} & 5\hat{b} \end{vmatrix}$ structure also occurs in the absence of further exposure, but the transformation takes ~10 hours. The apparent

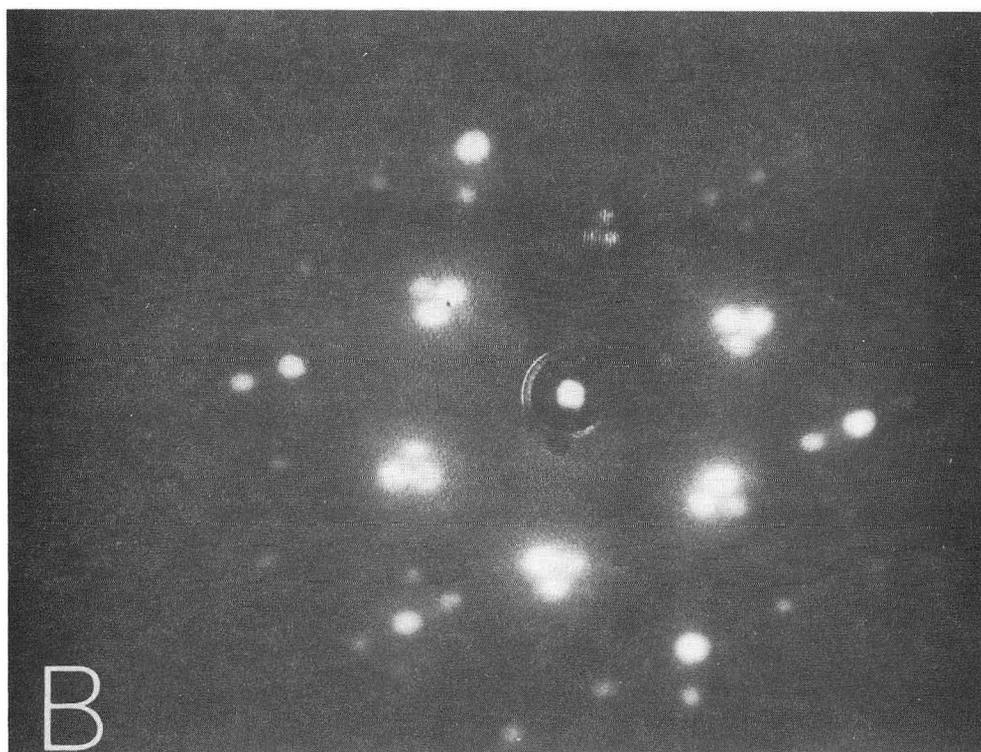
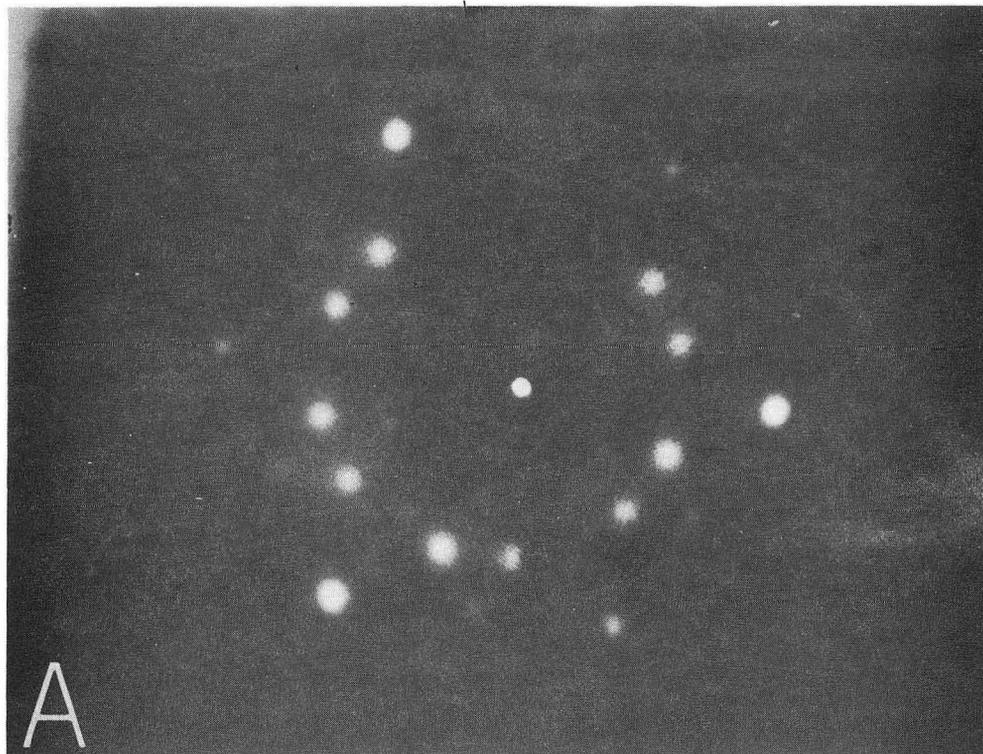
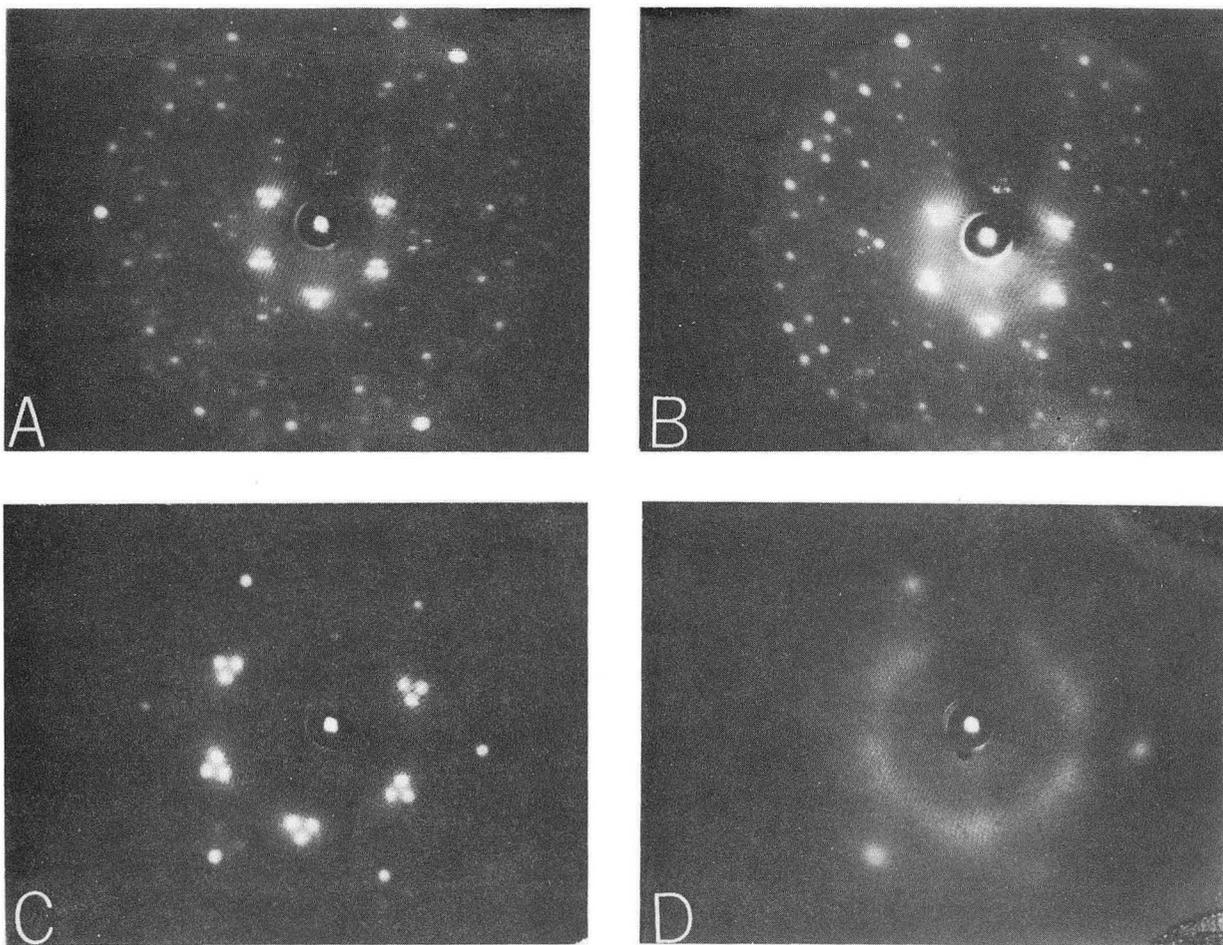


Figure 6 A) A LEED pattern of the Pt(111)- $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 4\hat{a} & 4\hat{b} \end{vmatrix}$ -Benzene structure at 29 volts.
B) A LEED pattern of the Pt(111)- $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 5\hat{a} & 5\hat{b} \end{vmatrix}$ -Benzene structure at 29 volts.



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Figure 7 A) A diffraction pattern for the $\text{Pt}(111)-\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 5\hat{a} & 5\hat{b} \end{vmatrix}$ -Benzene structure at 55 volts showing the first order diffraction beams of Pt(111).

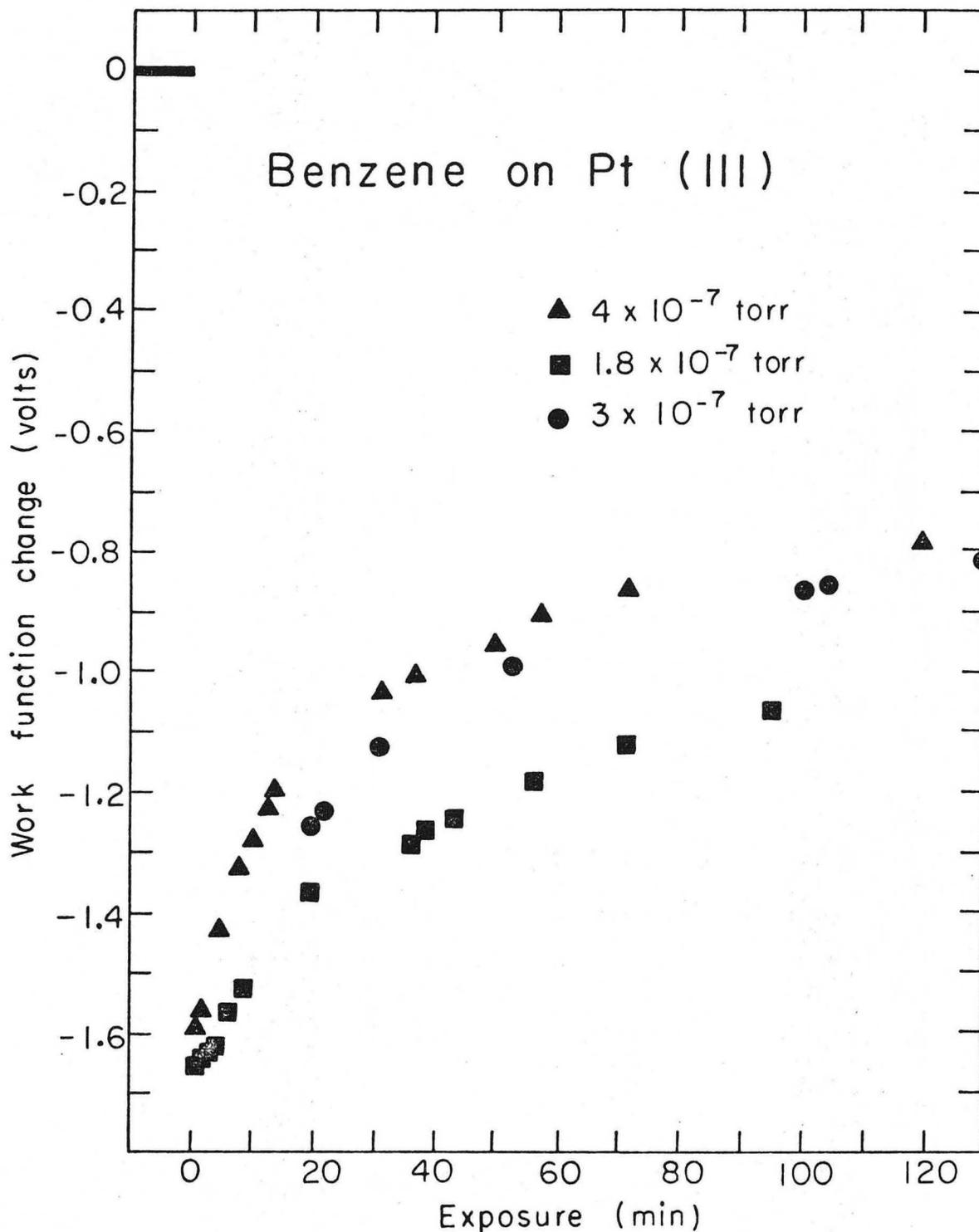
B) A diffraction pattern for the $\text{Pt}(111)-\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 5\hat{a} & 5\hat{b} \end{vmatrix}$ -Benzene structure at 48 volts showing the first order diffraction feature of the surface structure.

C) A diffraction pattern for the $\text{Pt}(111)-\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 5\hat{a} & 5\hat{b} \end{vmatrix}$ -Benzene structure at 29 volts.

D) A diffraction pattern taken at 29 volts after heating the $\text{Pt}(111)-\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 5\hat{a} & 5\hat{b} \end{vmatrix}$ -Benzene structure to 140°C in the presence of benzene flux.

hexagonal symmetry of the diffraction patterns occurs because 3 domains of these structures are possible. Observations have been made on patterns for which only two of the domains are predominant and the pattern did not show 6-fold symmetry. The work function shifts which accompany these structural changes are shown in Fig. 8. The work function change that occurs is quite dramatic since the exposures are very high (> 100 L) and the coverage of surface species would be expected to remain constant after a few seconds of exposure if no structural changes occurred. On initial adsorption the work function of the surface decreases very rapidly, goes through a minimum (~ -1.8 V), then increases slowly toward a higher, steady state value ($\sim -.7$ v). The initial ordered $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 4\hat{a} & 4\hat{b} \end{vmatrix}$ structure appears slightly after the minimum work function value has been reached ($\Delta\phi \sim -1.4$ v). The second ordered $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 5\hat{a} & 5\hat{b} \end{vmatrix}$ structure (Figs. 7A,B,C) forms after the work function has increased to ~ -1.0 V. The time required for the work function to reach the steady state value and for the $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 5\hat{a} & 5\hat{b} \end{vmatrix}$ structure to appear is dependent on the benzene pressure. At lower benzene fluxes, the time necessary to reach the steady state WFC and structure increases. Gentle heating of the Pt(111)- $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 5\hat{a} & 5\hat{b} \end{vmatrix}$ -Benzene structure to 140°C in the presence of large incident benzene flux disorders the surface structure (Fig. 7D).

Adsorption of benzene on the (100) crystal face of platinum causes the (5 \times 1) structure characteristic of the clean metal surface to disappear rapidly. A new diffraction pattern with 1/2 order circular streaks appears (Fig. 9A) indicative of a poorly ordered layer with



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Figure 8 Work function change as a function of exposure time for benzene on the Pt(111) surface. The pressures should be multiplied by 5.7 to give the effective pressure at the surface.

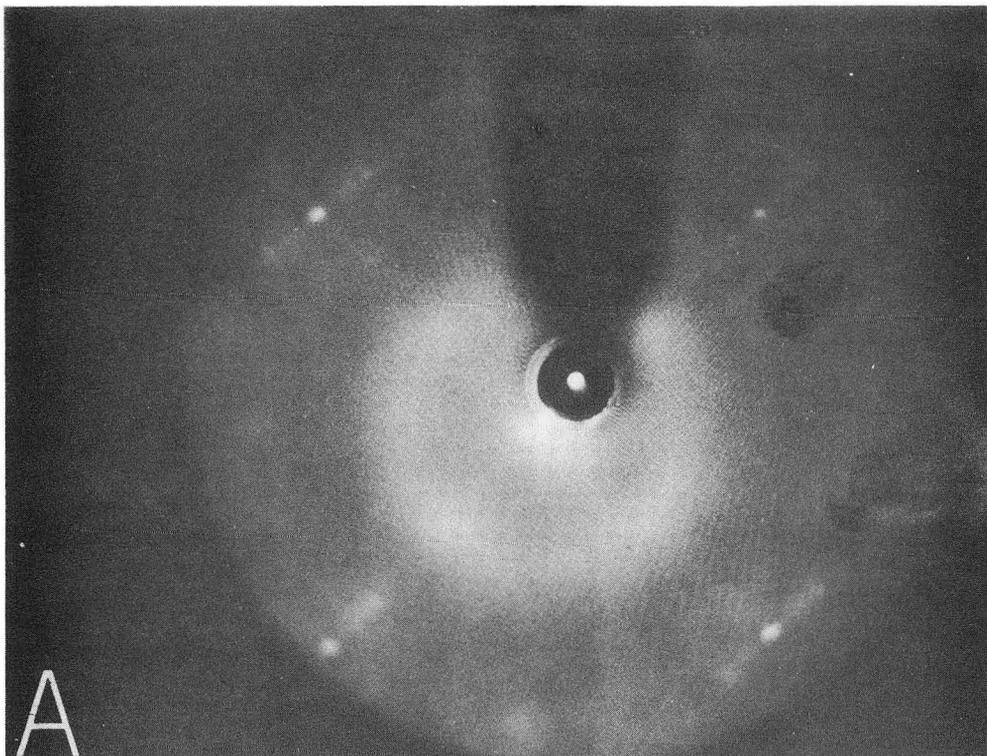
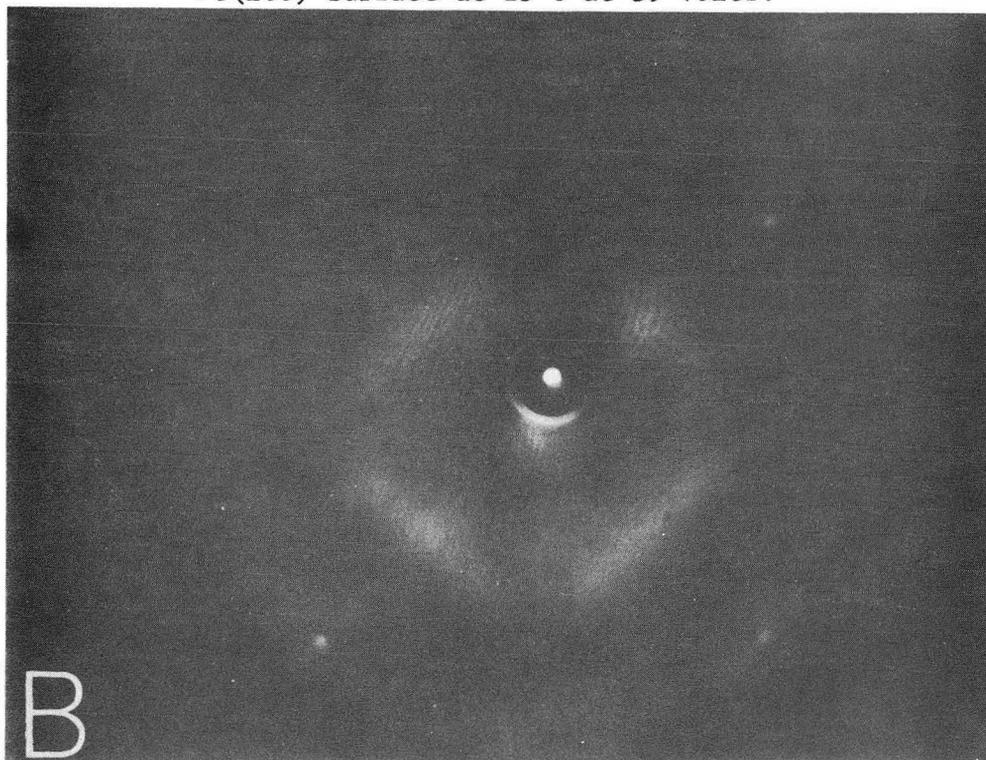


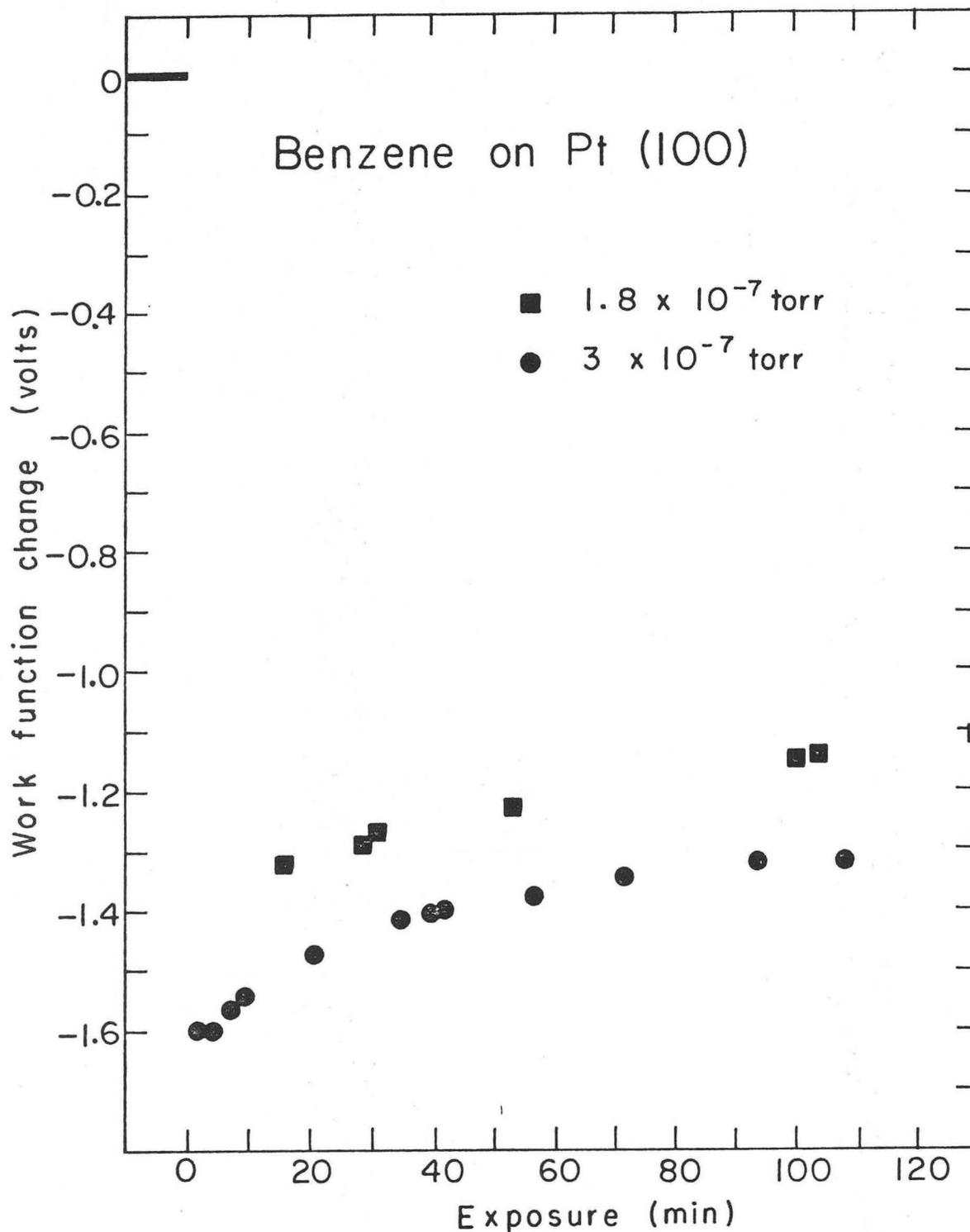
Figure 9 A) The diffraction pattern of benzene adsorbed on the Pt(100) surface at 25°C at 59 volts.



B) The diffraction pattern resulting from benzene adsorption on the Pt(100) surface after heating to 140°C with incident benzene flux at 59 volts. XBB 7211-5891

twice the spacing of the substrate. The work function change of the Pt(100) surface on adsorption of benzene is less sensitive to exposure than the Pt(111)-benzene system (as is shown in Fig. 10); however, the same type of increase in work function is observed. When the incident benzene flux is terminated the 1/2 order diffraction features disappear while the work function increases slightly. Upon heating in vacuo to 140°C the work function increased by .08 v and the 1/2 order ring like diffraction features disappeared. The ring like diffraction features (Fig. 9A) reappeared when the surface was exposure to benzene again at 25°C. Upon heating to 140°C for a short period with incident flux the LEED pattern shows a set of 1/2 order streaks (Fig. 9B) which indicate the surface is more ordered than it had been previously. The work function of this structure was -1.2 v and it is stable to further exposure or evacuation.

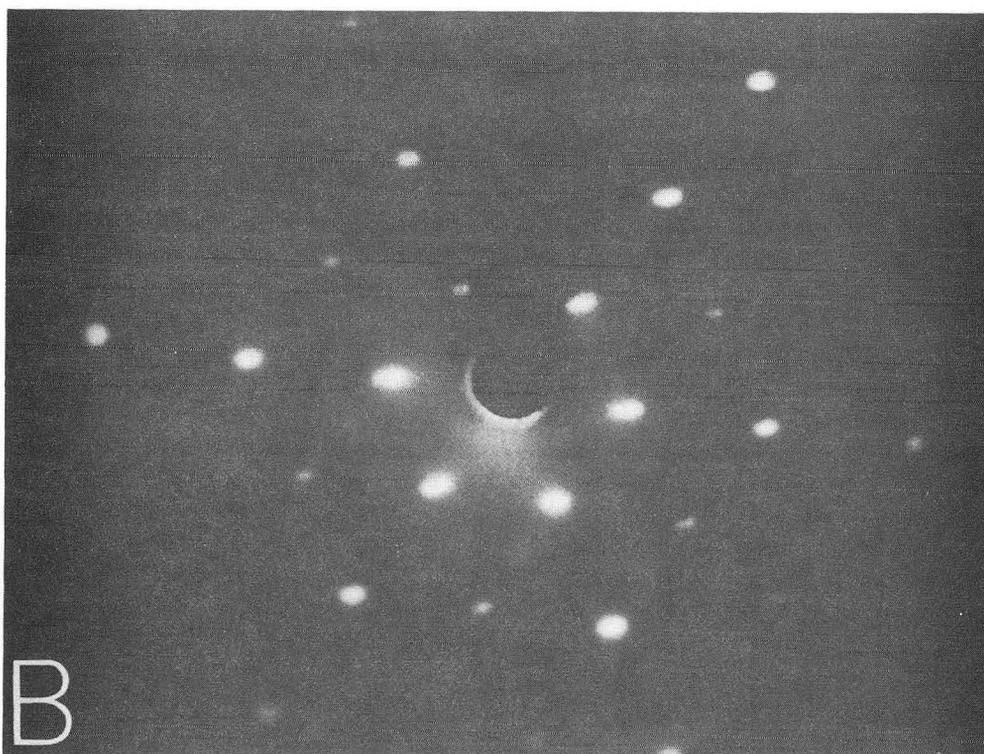
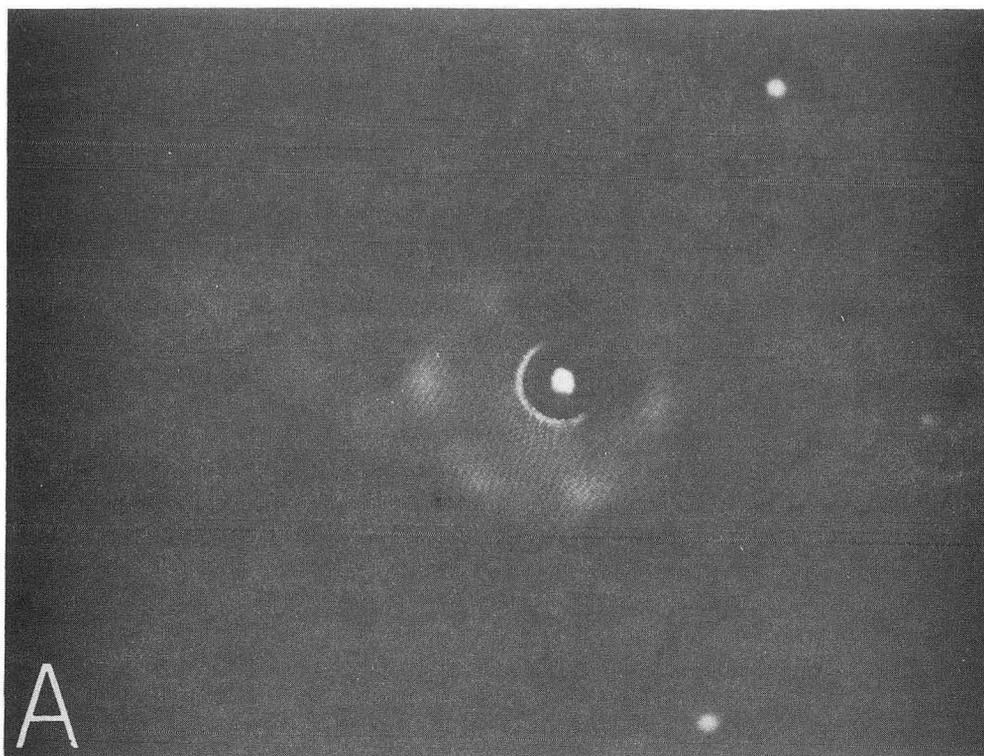
Naphthalene adsorption: Naphthalene adsorbed on the Pt(111) surface at 140°C forms a (6×6) structure that is shown in Fig. 11B. The work function change that accompanies this ordered adsorption is $\Delta\phi = -2.0$ V. When adsorbed at room temperature the degree of order in the naphthalene layer and the work function change depend on the exposure rate. A typical diffraction pattern is shown in Fig. 11A. Large exposure rates (.4 L/sec) lead to poor order (eg. a diffuse (3×3) pattern) and increased values of $\Delta\phi$ (Fig. 12 and 13). With gentle heating to 150°C the adsorbed layer becomes more ordered and there is a transformation from the (3×3) to the (6×6) surface structure. Simultaneously the work function decreases (Fig. 13).



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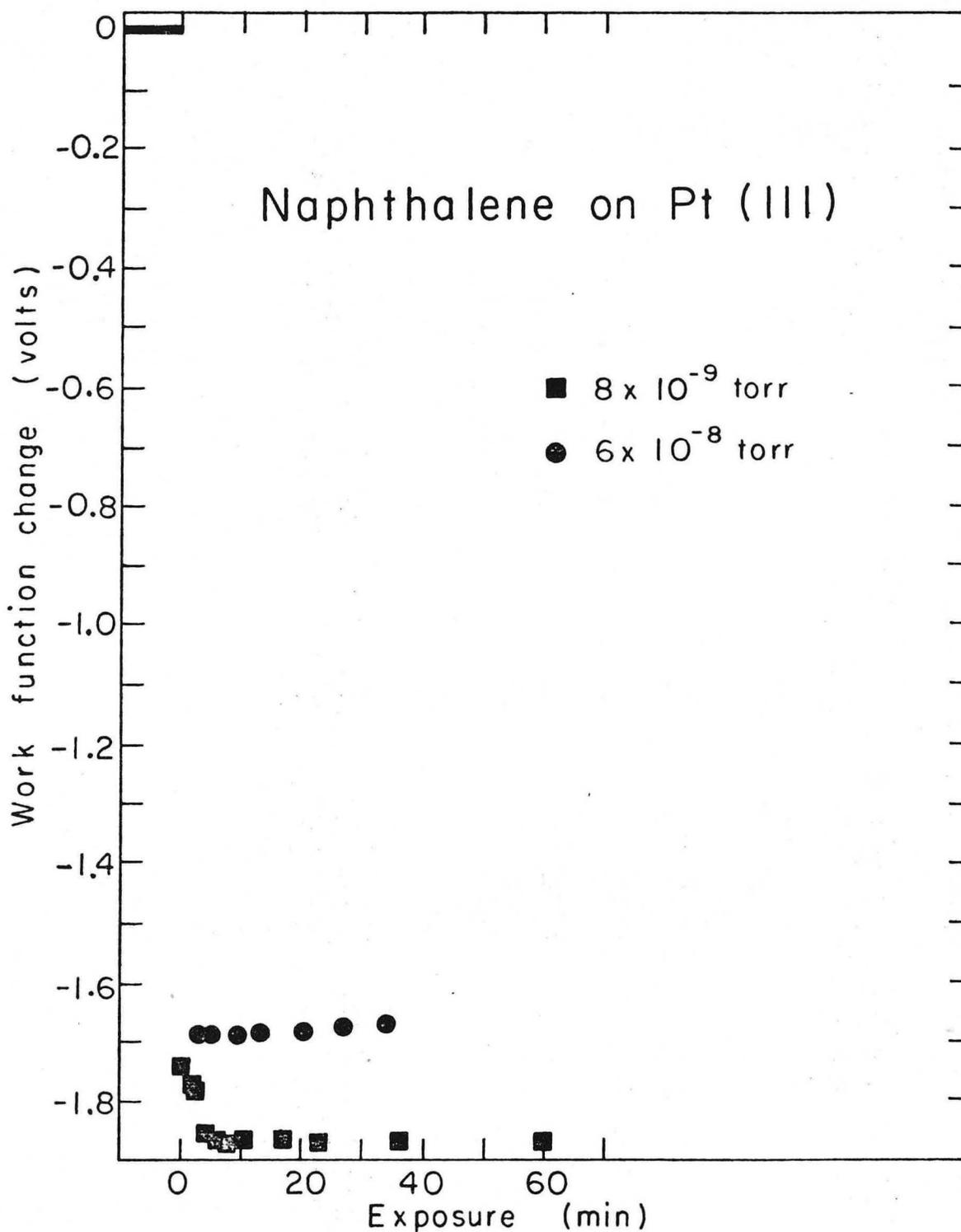
Figure 10 Work function change as a function of exposure for benzene adsorption on the Pt(100) surface. The pressures should be multiplied by 5.7 to give the effective pressure at the surface.

- Figure 11
- A) The diffraction pattern at 52 volts resulting from naphthalene adsorption on the Pt(111) surface. The system pressure was 9×10^{-9} torr corresponding to an exposure rate of approximately .05 L/sec.
- B) A diffraction pattern of the Pt(111)-(6×6)-Naphthalene structure at 52 volts. The sample had been heated to 150°C in vacuum after exposure.



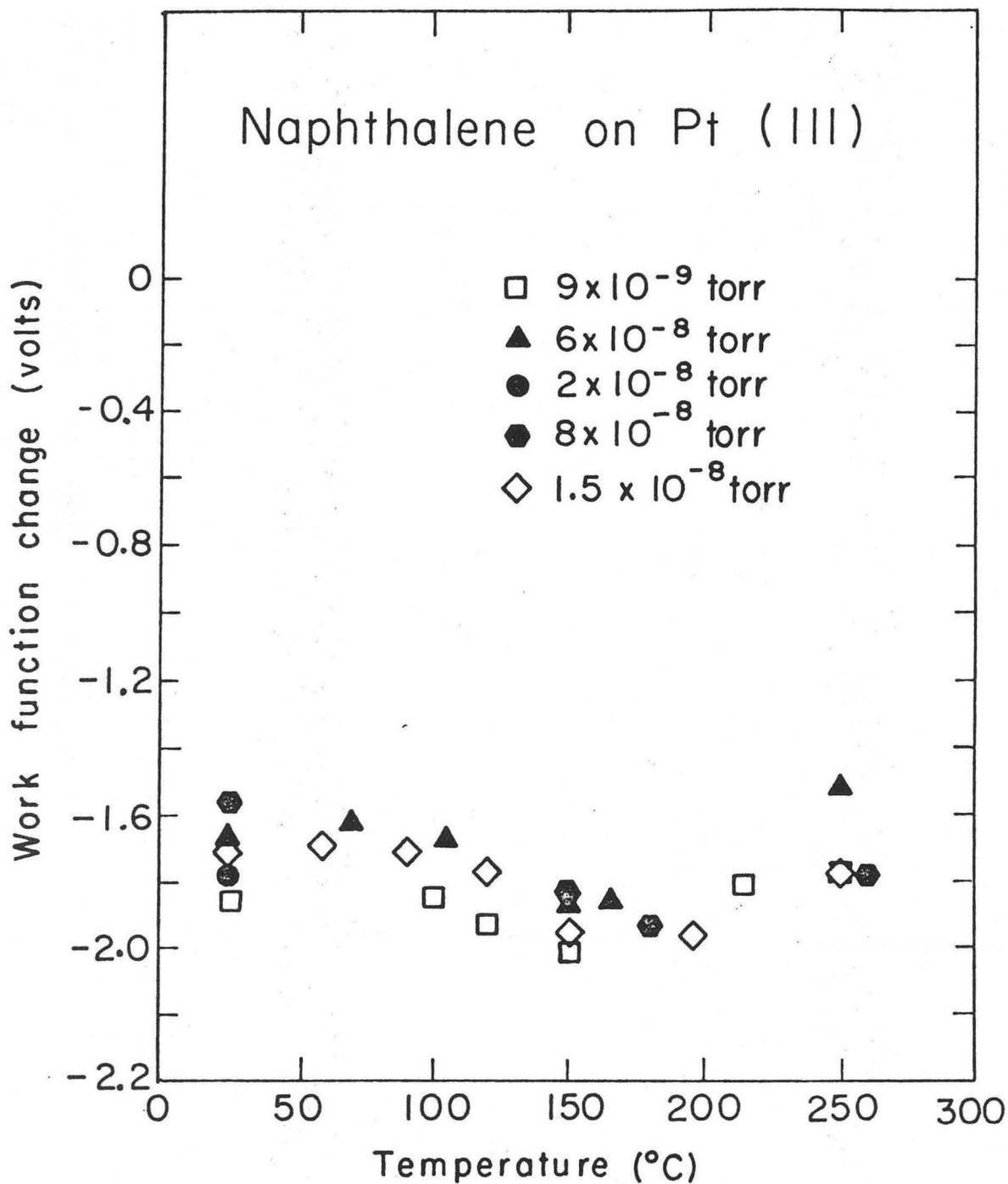
XBB 7211-5894

Fig. 11



XBL7210-4205A

Figure 12 The work function change as a function of exposure for naphthalene adsorbed on the Pt(111) surface. The pressures should be multiplied by 6 to yield effective pressures at the surface.



XBL7210-4210A

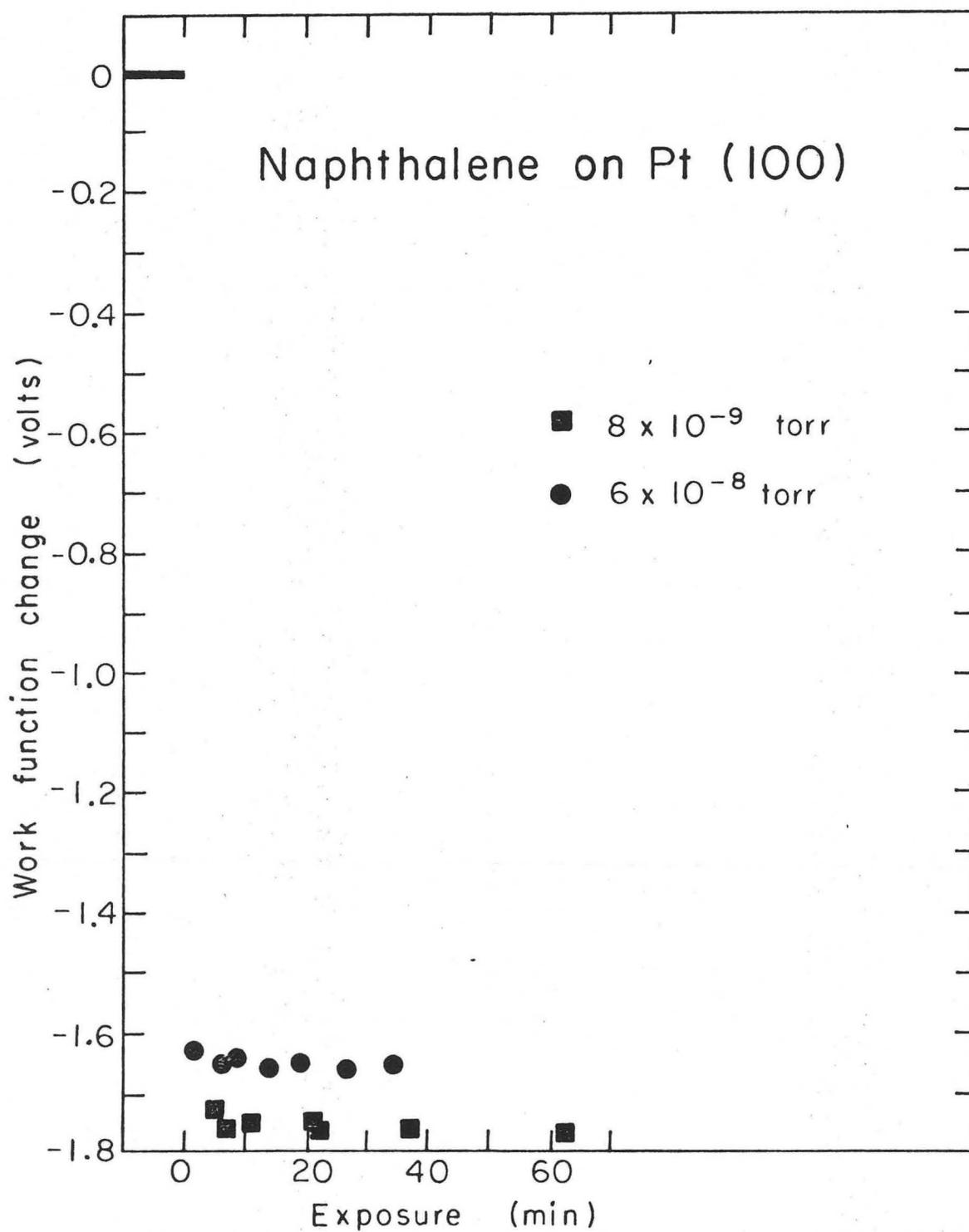
Figure 13 Work function change as a function of temperature for naphthalene adsorbed on the Pt(111) surface. The pressures should be multiplied by 6 to yield effective pressures at the surface. Heating was carried out in vacuum after initial exposure.

On the Pt(100)-(5×1) surface naphthalene adsorption causes a rapid disappearance of the (5×1) surface structure and an increase in background intensity. The work function change on adsorption is ~ -1.75 v, but is again sensitive to initial exposure rates (Fig. 14). The work function change as a function of temperature is shown in Fig. 15. The LEED pattern did not show any evidence for the formation of an ordered structure under the experimental conditions utilized (temperature = 25°C to 150°C, pressure = 1×10^{-8} to 6×10^{-8} , exposures $< 10^4$ L).

Pyridine adsorption: Pyridine adsorbed on the Pt(111) surface produces a very poorly ordered surface structure; the dimensions of the overlayer are twice as large as those of the substrate unit cell. The work function change on adsorption is ~ -2.7 v; however, both the work function change and the degree of ordering are sensitive to initial exposure rates (Fig. 16). With lower pyridine fluxes the adsorbed layer is more ordered and the work function change is more negative.

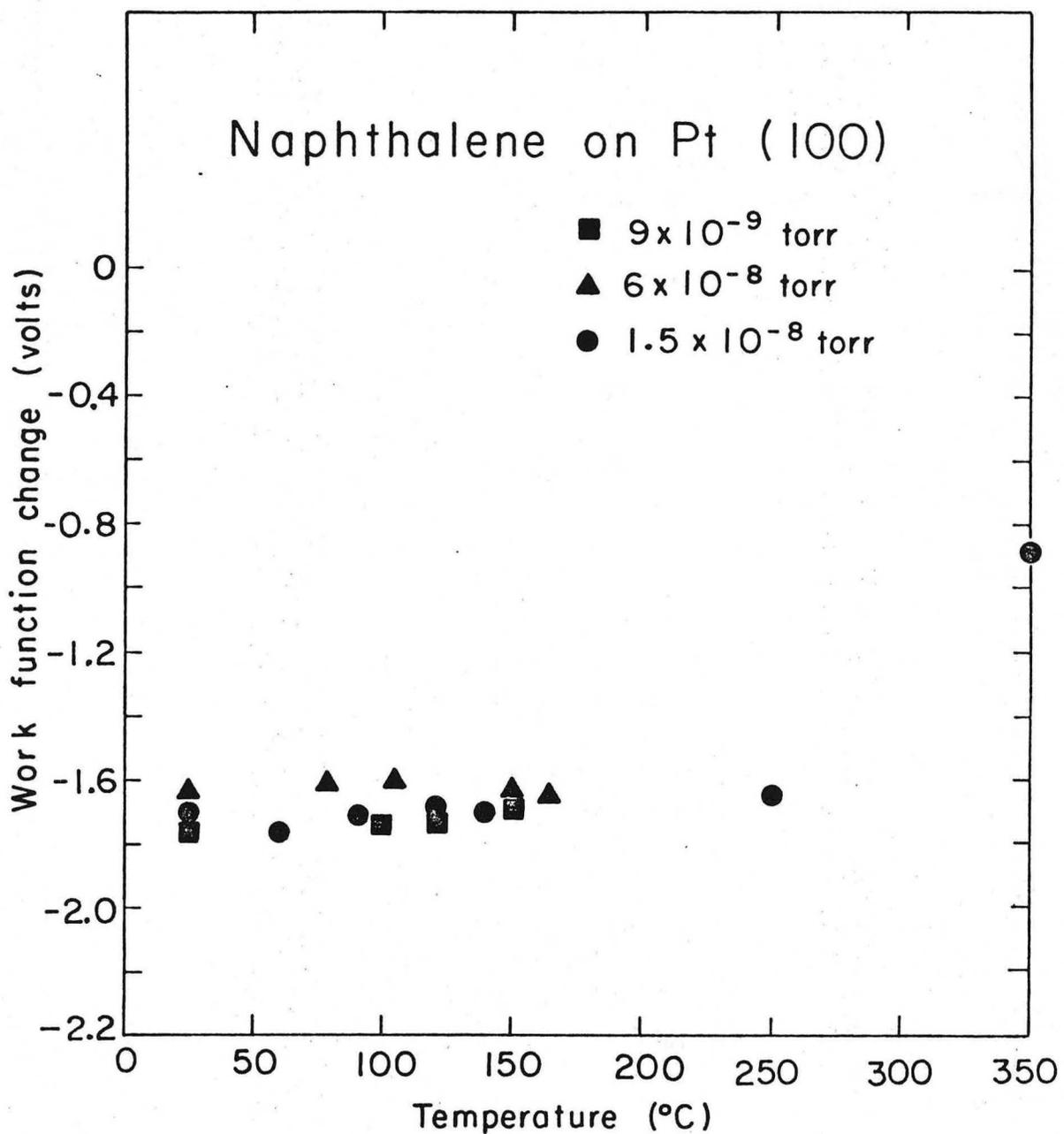
By heating the adsorbed layer to 250°C a new surface structure is formed. The overlayer exhibits one-dimensional order with a spacing three times the size of the underlying lattice. This pattern is shown in Fig. 17B. Accompanying this change in structure is a decrease in the magnitude of the work function change from -2.7 v to -1.7 v. This structure can also be obtained by exposing a clean Pt(111) surface to pyridine at 250°C.

Pyridine adsorbed on the Pt(100)-(5×1) surfaces at 25°C gives rise to a poorly ordered structure which is characterized by a (1×1)



XBL7210-4202

Figure 14. Work function change as a function of exposure for naphthalene adsorbed on the Pt(100) surface. Pressures should be multiplied by 6 to yield effective pressures at the surface.



XBL7210-4214A

Figure 15 Work function change as a function of temperature for naphthalene adsorbed on the Pt(100) surface. The pressures should be multiplied by 6 to yield effective surface pressures. Heating has been carried out in vacuum after initial exposure.

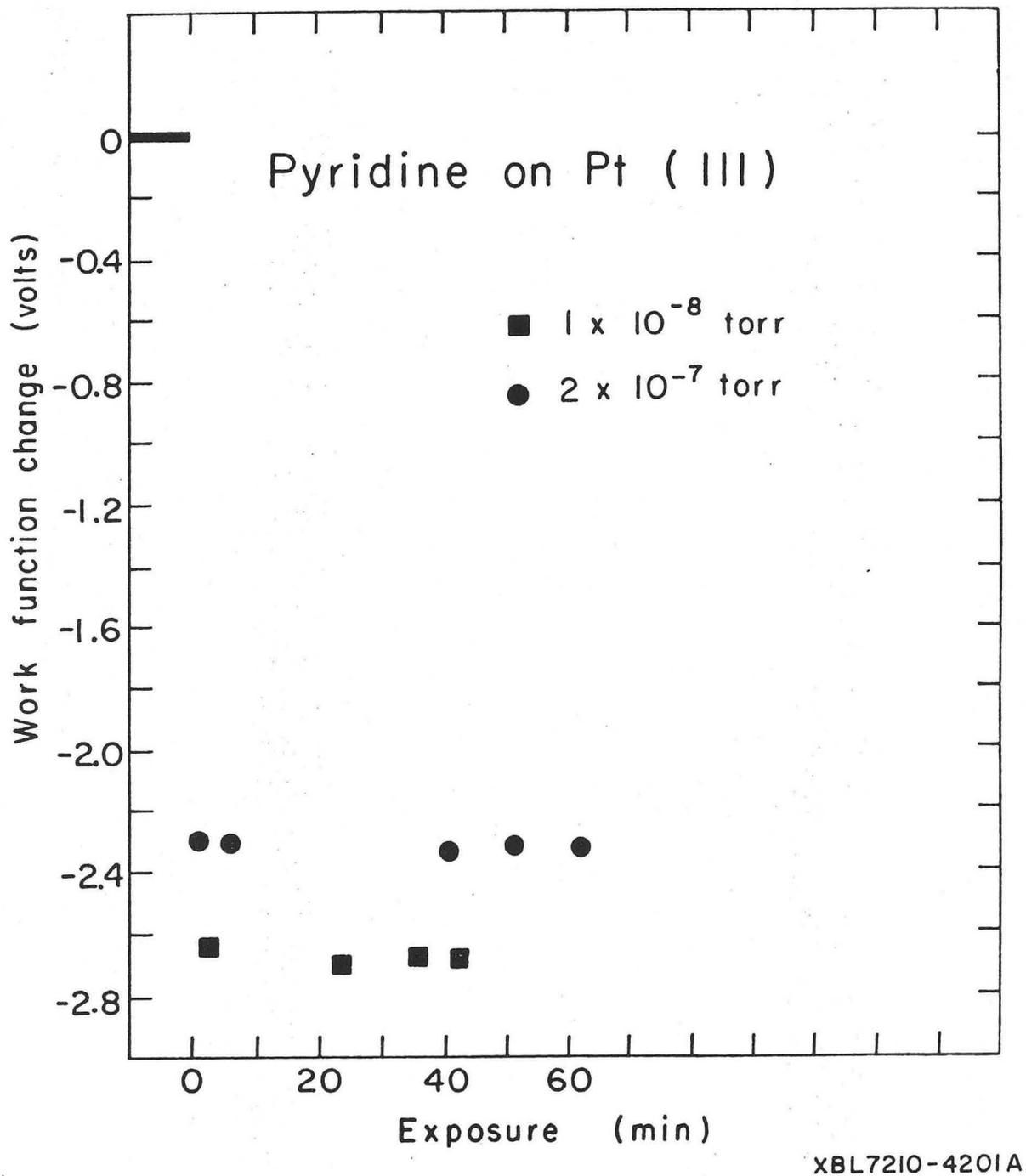
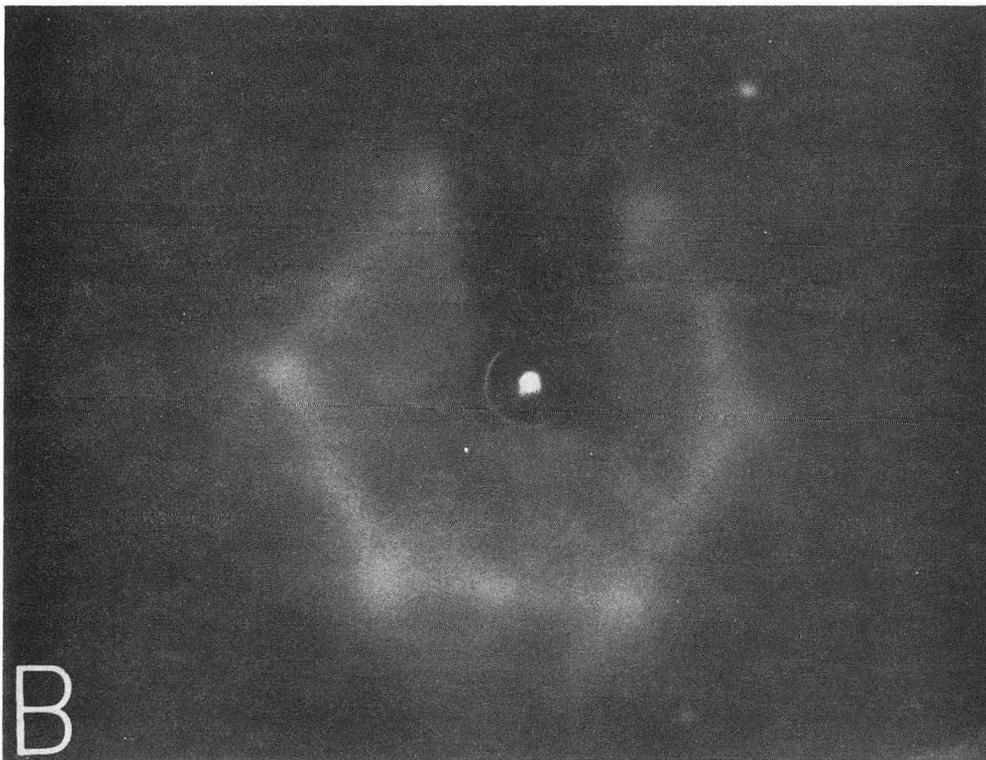


Figure 16 Work function change as a function of exposure for pyridine adsorption on the Pt(111) surface. The pressure should be multiplied by 6 to yield effective surface pressure.

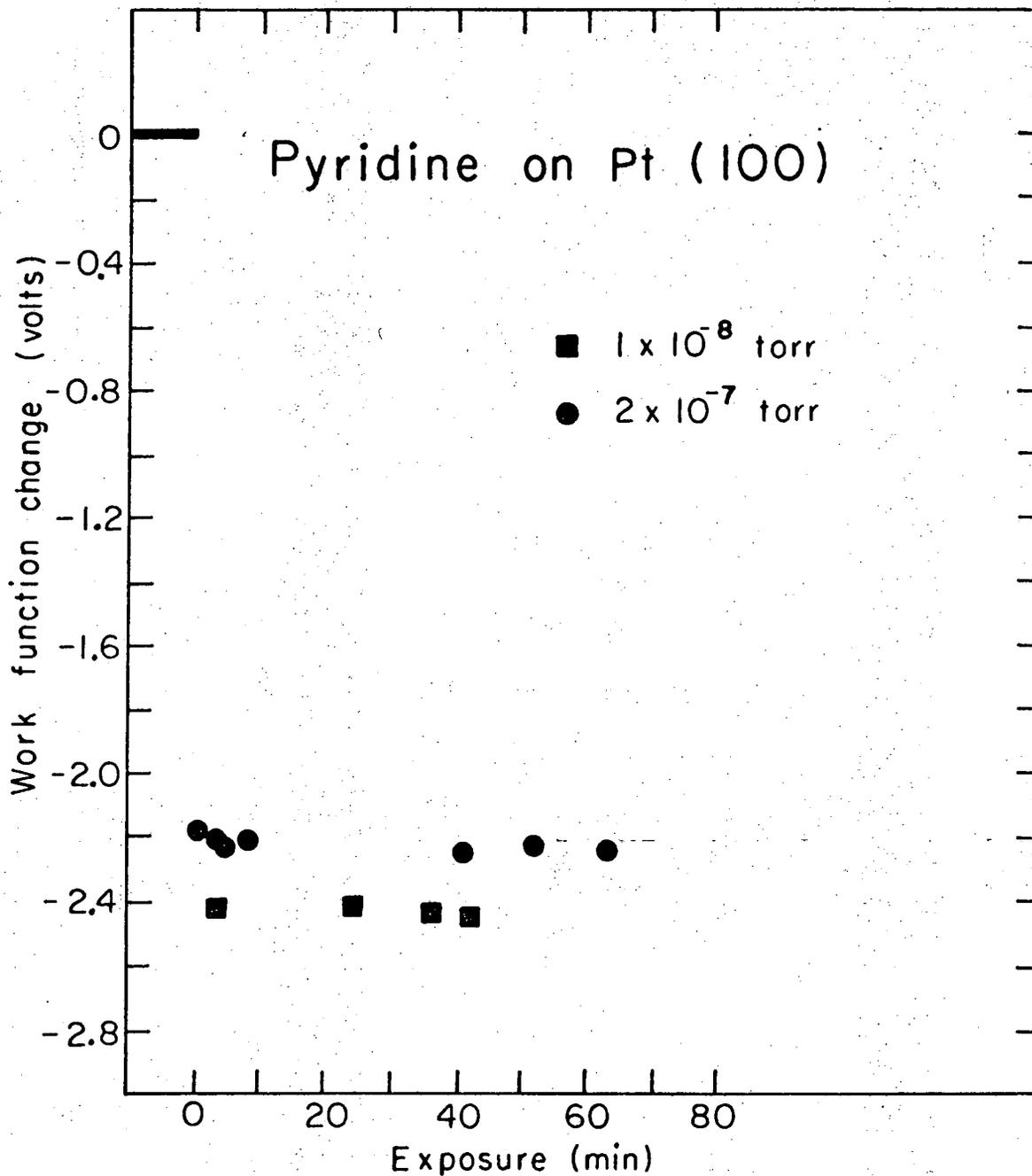
- Figure 17
- A) The diffraction pattern resulting from pyridine adsorption on the Pt(100) surface taken at 60 volts after heating the sample to 250°C in vacuum after initial exposure at 25°C.
 - B) The diffraction pattern resulting from pyridine adsorption on the Pt(111) surface taken at 53 volts after heating the sample to 250°C in vacuum after initial exposure at 25°C.



diffraction pattern with very high background intensity. The work function change on adsorption is ~ -2.4 v; however, this value depends on the initial rate of adsorption (Fig. 18). Higher initial exposure rates give smaller work function changes. Heating to 250°C causes the appearance of a poorly ordered $(\sqrt{2}\times\sqrt{2})\text{R-}45^\circ$ diffraction pattern (Fig. 17A).

Discussion

Benzene first forms a disordered layer on the Pt(111) surface but with further exposure the Pt(111)- $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 4\hat{a} & 4\hat{b} \end{vmatrix}$ -Benzene structure is formed (Fig. 6A). Continued exposure results in the transformation of this surface structure to the Pt(111)- $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 5\hat{a} & 5\hat{b} \end{vmatrix}$ -Benzene surface structure (Figs. 7A, B, C). The first, $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 4\hat{a} & 4\hat{b} \end{vmatrix}$ structure forms shortly after the minimum in the work function has been reached ($\Delta\phi \sim -1.4$ V). After the minimum has been passed the work function increases toward a steady state value of ~ -0.7 v. The $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 5\hat{a} & 5\hat{b} \end{vmatrix}$ structure forms when the work function is about -1.0 v. This correlation between the transformation of the benzene surface structure and the change in work function suggests that the orientation of the adsorbed benzene molecules is changing markedly as a function of increased exposure. The diffraction information indicates a change in the packing of the adsorbed ordered benzene layer. A decrease in the density of the adsorbed layer during the order-order phase transformation is not possible because of the high flux (.5 L/sec) incident on the crystal throughout some of these experiments. In fact, the density of the adsorbed layer is



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Figure 18 Work function change as a function of exposure for pyridine adsorbed on the Pt(100) surface. Pressure should be multiplied by 6 to yield the effective surface pressure.

increasing during continued exposure, as indicated by the observation that higher incident benzene fluxes cause the transformation from one benzene surface structure to another to occur more rapidly. The work function change indicates that there is a decrease in the magnitude of the charge transfer occurring as the density of the adsorbed layer increases. If the adsorbed species retained the same bonding characteristics during the transformation and the coverage increased, the work function would decrease. Thus, the increasing density accompanied by an increase in the work function can only be explained by assuming that the area per adsorbed molecule must be decreasing. The criteria for the transition are then: 1) the area of the adsorbed species must decrease, and 2) the charge transfer must decrease. A likely model consistent with these criteria is that the initial adsorption involves a benzene adsorbed with its ring at some small angle to the surface (Fig. 19). The final adsorbed state may involve reoriented benzene molecules adsorbed with their rings at a large angle or perpendicular to the surface (Fig. 20). The "initial" adsorbed species would be held on the surface by a π bond to the aromatic ring similar to the bonds in the so called "sandwich compounds".¹² Since the metal surface is highly electron deficient ($\phi_{Pt} = 5.4$ v), a large induced dipole would be expected in the adsorbed layer.

The $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 5\hat{a} & 5\hat{b} \end{vmatrix}$ structure which forms at large exposures may involve benzene molecules adsorbed with their rings perpendicular to the surface (Fig. 20). For this type of adsorption to occur the benzene must either lose a hydrogen or its aromaticity. Recent exchange studies

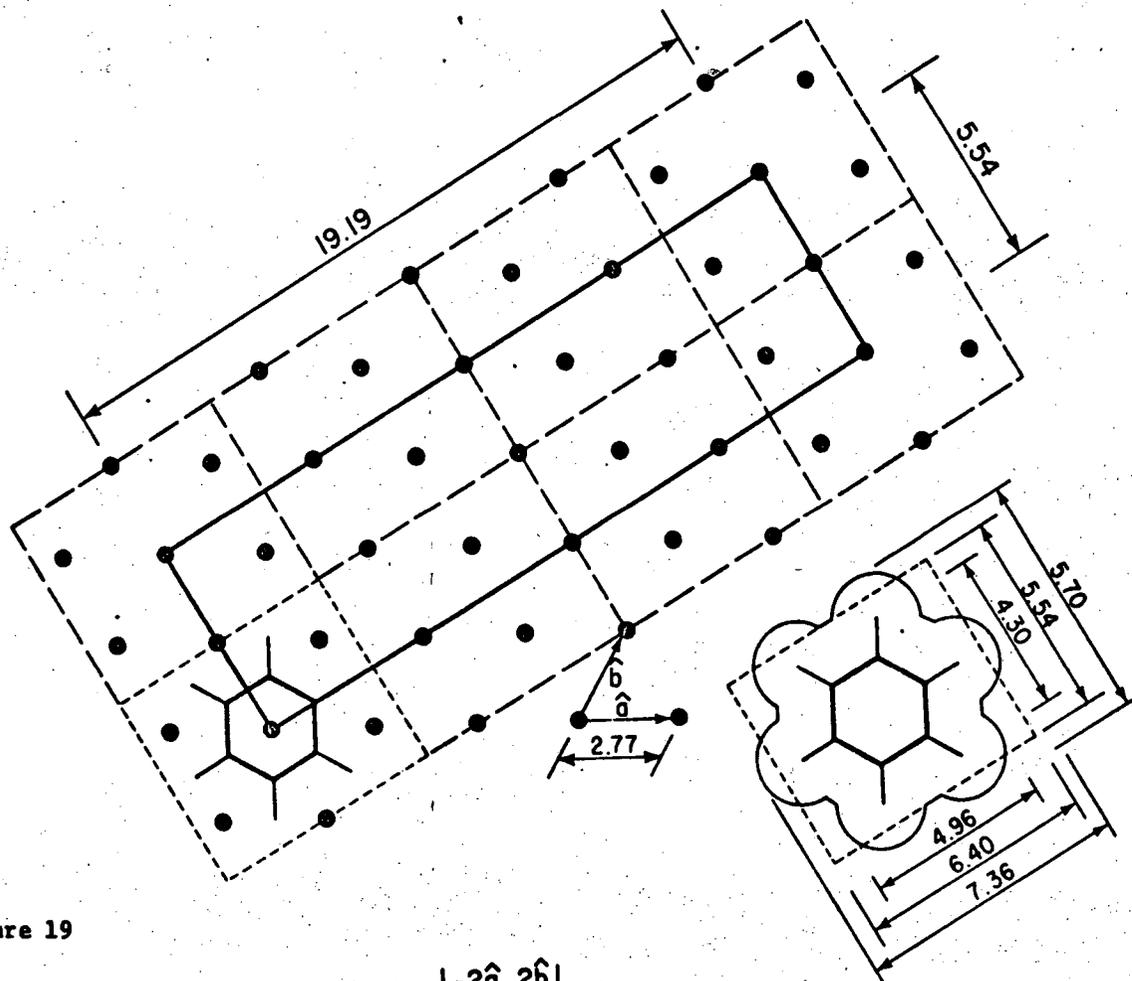
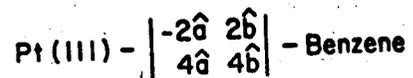


Figure 19



A schematic diagram of the unit cell of the Pt(111) - $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 4\hat{a} & 4\hat{b} \end{vmatrix}$ - Benzene structure divided into areas containing a single benzene molecule. The relative position of the adsorbate

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unit cell and the substrate unit cell is uncertain. The benzene is shown parallel to the surface for convenience; it may actually be rotated by some angle relative to the surface. All dimensions are in angstroms.

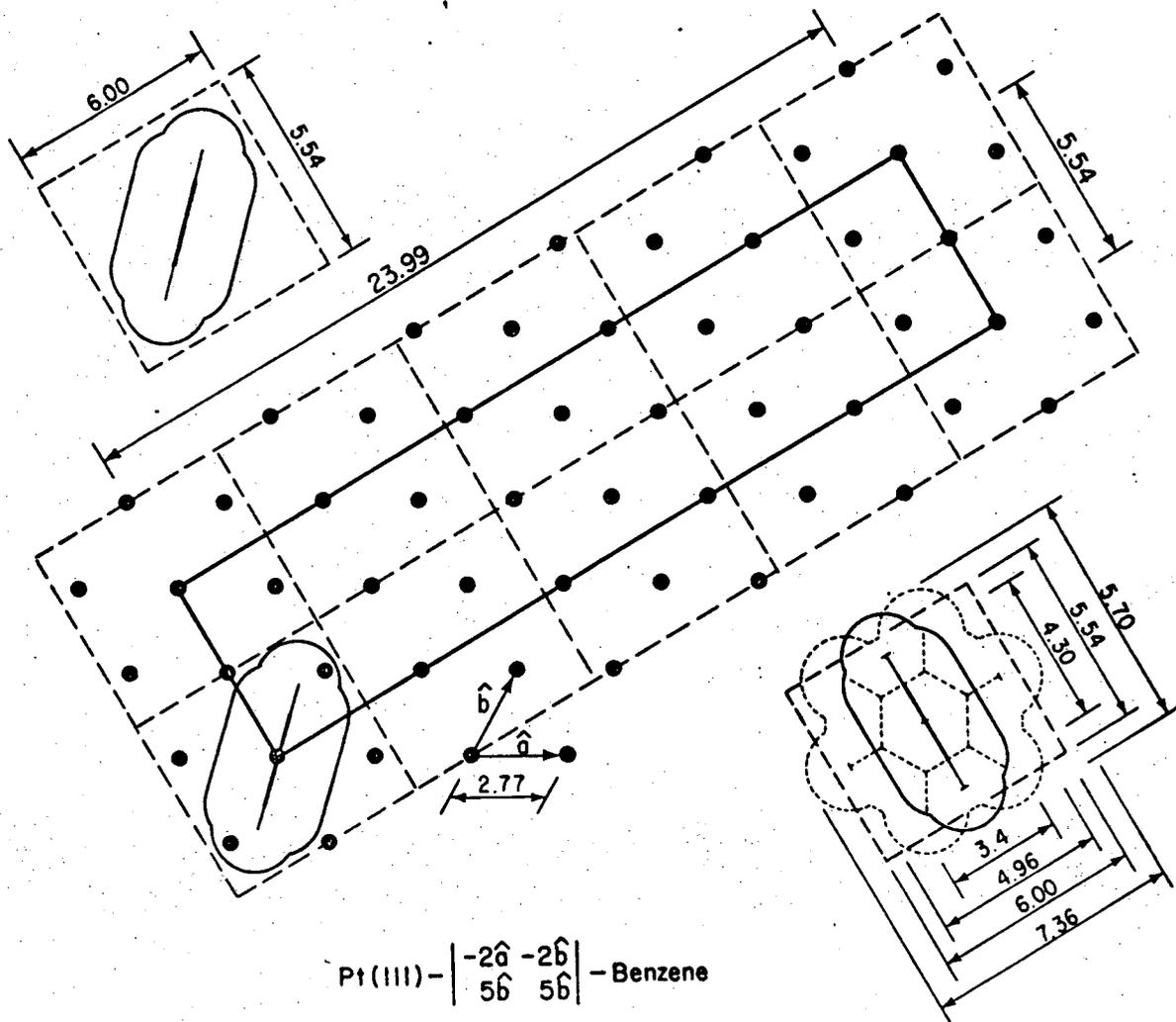
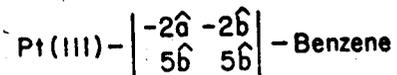


Figure 20



A schematic diagram of the unit cell for the Pt(111)-

Benzene structure divided into areas which contain a single benzene molecule. The benzene is shown in several orientations; the most likely is shown in the top left hand corner

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of the figure. The position of the adsorbate unit cell relative to the substrate unit cell is uncertain. All dimensions are in angstroms.

between perdeuterobenzene and benzene on Pt films have shown rapid exchange of hydrogen and deuterium between these species. These workers postulate a dissociation of the benzene (without loss of aromaticity) and loss of hydrogen atoms to form a singly bonded intermediate.¹³ Thus the adsorbed species which gives the $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 5\hat{a} & 5\hat{b} \end{vmatrix}$ structure is most likely a singly dehydrogenated benzene molecule covalently bonded to the surface. This type of reorientation satisfies both criteria for the surface transformation. That is, the surface area occupied by the adsorbed species certainly decreases, and the amount of charge transfer decreases as well. The charge transfer would be expected to decrease for two reasons: 1) The thickness of the adsorbed layer increases while the electronegativity of the substrate remains the same; therefore the strength of the induced dipole in the benzene layer would decrease. 2) The "back donation" of electrons involved in a covalent bond would decrease the effective induced dipole at the surface.

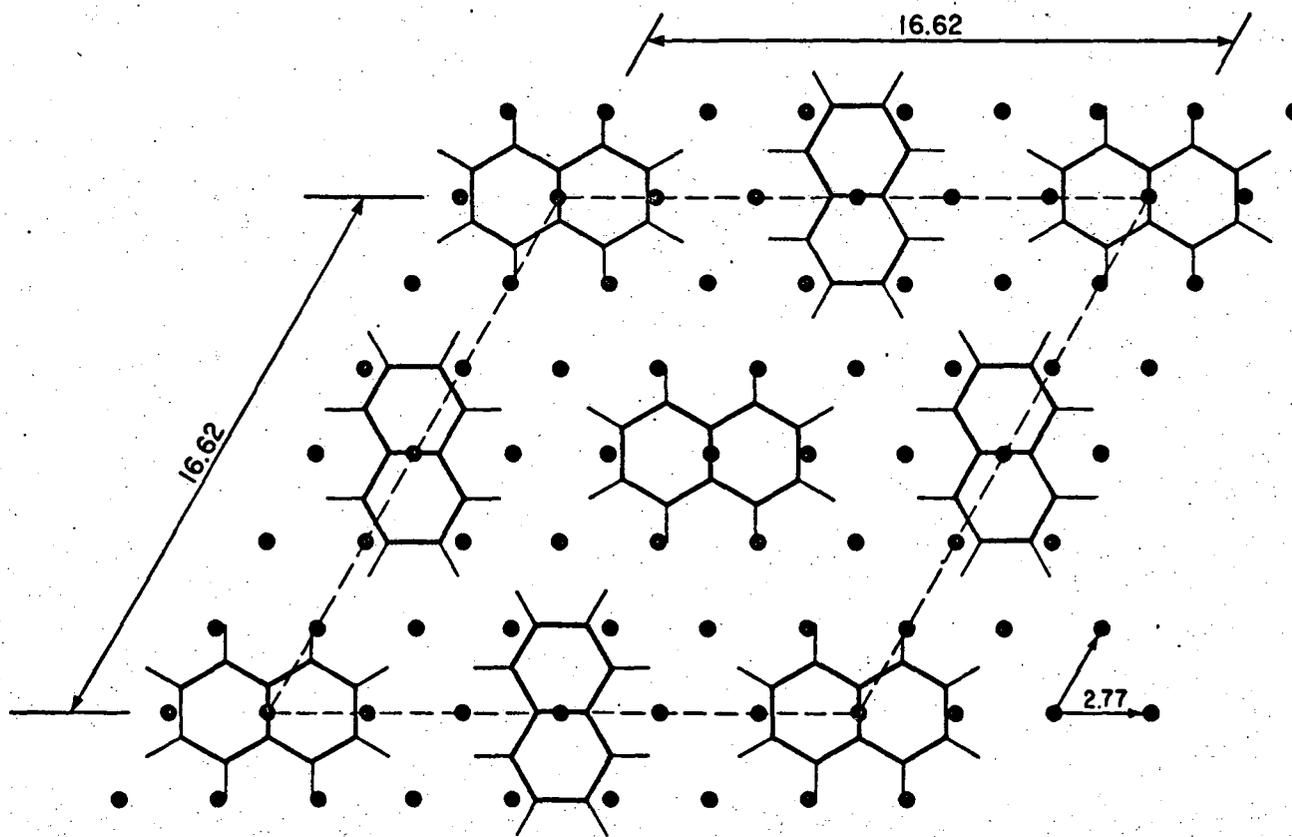
Analysis of the diffraction information yields only the translational unit vectors of the adsorbed surface layer. The position of the unit vectors in the adsorbed layer relative to the underlying unit vector has not been determined uniquely; likewise the number of adsorbate molecules per unit cell has not been determined uniquely. Rigorous answers for both of these questions await the development of structure analysis techniques utilizing LEED intensity data.

The number of adsorbate molecules per unit cell has been determined by applying the two criteria above and using the crystallographic information available for the system. This includes the size of the

clean substrate unit cell, the size of the adsorbate-induced unit cell, the symmetry of the adsorbate-induced unit cell, and the size and symmetry of the adsorbate molecule. The first criterion is that the number of equivalent adsorbate molecules per unit cell should not lead to a reduction in the unit cell size. For instance, if the unit cell $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 4\hat{a} & 4\hat{b} \end{vmatrix}$ contained 2 benzenes in equivalent positions the unit cell size would be reduced to $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 2\hat{a} & 2\hat{b} \end{vmatrix}$. The second criterion is that the adsorbed layer must be fairly uniform over the surface; in particular the surface should not contain large unoccupied areas and the interaction energy between each adsorbed molecule in a given structure and the substrate should be similar. Using these criteria, we postulate the benzene surface structures that are shown in Figures 20 and 21 to explain the observed experimental data. The position of the adsorbate unit cell relative to the substrate unit cell is uncertain. However, there is sufficient evidence to indicate that the postulated number of benzene molecules per unit cell is correct.

The adsorption of naphthalene on the Pt(111) surface at 150°C causes the formation of a well defined (6×6) structure. The work function change (WFC) on adsorption is ~-2.0 v. This large work function change indicates a large induced dipole moment in the adsorbed layer. Therefore it seems likely that the naphthalene ring system is parallel or at some small angle to the plane of the metal surface. Adsorption of naphthalene at 25°C causes the formation of a poorly ordered (3×3) structure (WFC ~ -1.8±.1 v). The degree of ordering and WFC depend on the rate of exposure; the lower the exposure rate the better the

order and the more negative the work function change. However, heating any of these poorly ordered structures to 150°C causes the appearance of the Pt(111)-(6×6) naphthalene structure and causes the work function change to approach -2.0 v. These phenomena seem to indicate that naphthalene has a large heat of adsorption and low mobility on the surface. The adsorbed layer may order on heating to 150°C because the mobility of the adsorbed species increases, that is, the poorly ordered surface structure may be annealed at the higher temperature. The fact that better order results from low initial exposure rates seems to indicate that ordering on the surface is also aided by slow "crystallite" growth, i.e., the growth of ordered domains of naphthalene. The transition required for the formation of the (6×6) diffraction pattern from the apparent (3×3) diffraction pattern may be either an increase in domain size or an actual change in the adsorbed structure probably corresponding to a rotation in the plane of the surface of half of the naphthalene molecules (as shown in Fig. 21) for which the angle of rotation has been arbitrarily chosen to be 90°. Naphthalene adsorbed with its ring system parallel or nearly parallel to the surface fits into the (3×3) structure (one molecule per unit cell) and the (6×6) structure (two molecules per unit cell). Since the work function indicates that a large dipole is induced in the adsorbed layer, it seems reasonable that naphthalene π bonds to the surface through its aromatic ring. The structure we have proposed in Fig. 21 is based on our best estimates of the number of naphthalene molecules per unit cell and the position of the adsorbed unit cell relative to the substrate



Pt(111) - (6x6) - Naphthalene

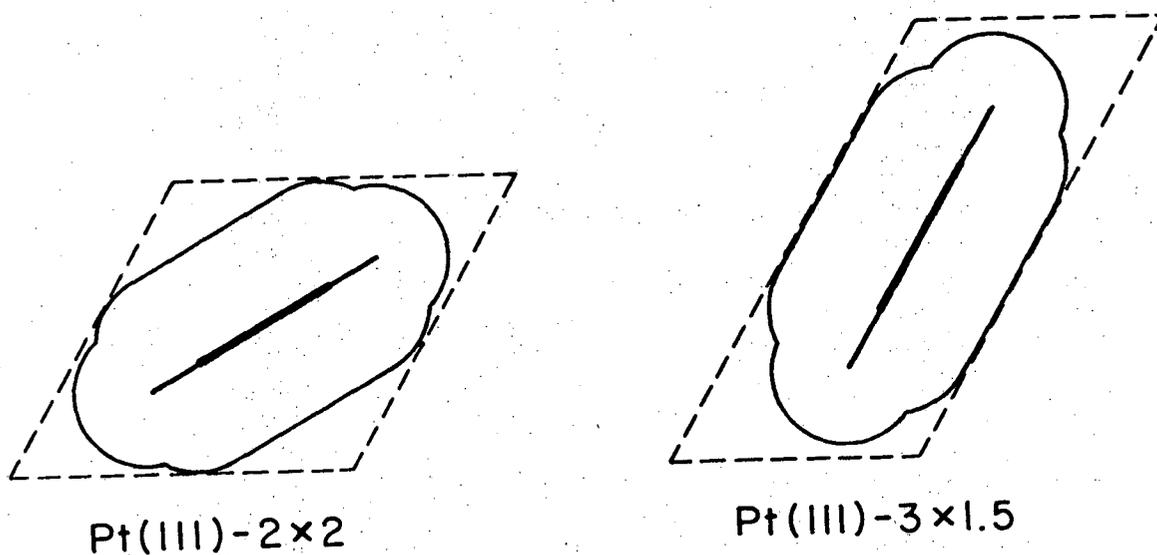
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Figure 21

A schematic diagram of the unit cell of the Pt(111)-(6x6) Naphthalene structure with the probable arrangement of naphthalene molecules in the unit cell. The angle of rotation of one set of parallel naphthalene molecules with respect to the other parallel set is uncertain.

unit cell. The position of the adsorbate unit cell relative to the substrate unit cell is uncertain since we have little information about the details of the interaction potential. However, there is sufficient evidence to corroborate the postulated number of naphthalene molecules per unit cell.

Pyridine adsorbed on the Pt(111) surface at 25°C forms a very poorly ordered structure with a characteristic distance two times the size of the underlying lattice. The work function change on adsorption is ~ -2.4 v. Because of the large work function change on adsorption the nitrogen lone electron pair must be involved in the bonding. This result is confirmed by recent experiments with 2,6-dimethylpyridine and 3,5-dimethylpyridine. The nitrogen lone electron pair is sterically hindered from interaction with the surface in 2,6-dimethylpyridine;¹⁴ 3,5-dimethylpyridine was used to check for the influence of other effects such as the size of the molecule and electron density changes with methyl substitution. With adsorption on Pt(111) and Pt(100) the magnitude of the work function change induced by 2,6-dimethylpyridine adsorption was .7 v smaller than the change induced by 3,5-dimethylpyridine adsorption. The work function changes for 3,5-dimethylpyridine were similar to those observed for pyridine. Since the nitrogen is certainly active during adsorption, the plane of the molecule might be expected to be at some large angle to the surface. Perpendicular adsorption of the pyridine through its nitrogen causes the pyridine to have an area comensurate with the formation of a (2x2) structure (Fig.22).



Pyridine

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Figure 22 A schematic representation of possible pyridine orientations on the Pt(111) surface. The Pt(111)-(2x2) diagram corresponds to pyridine adsorbed through its nitrogen. The Pt(111)-3x1.5 diagram corresponds to singly ortho-dehydrogenated pyridine adsorbed through both its nitrogen and the dehydrogenated ortho site.

If the adsorbed pyridine layer is heated to 250°C a new structure forms, characterized by one dimensional order with the unit vector in the overlayer being three times as long as the unit vectors in the substrate lattice (Fig. 22). The work function change becomes smaller ($\Delta\phi \sim -1.5$ v) indicating either: 1) an increased "back donation" from the substrate, 2) a less favorable geometry for the nitrogen lone pair interaction, or 3) an increase in the thickness of the adsorbed layer. Since the diffraction pattern seems to indicate an increase in the area per molecule (since the unit cell size increases) a significant contribution from 3) is not likely. Exchange studies with pyridine have indicated that the ortho position is very susceptible to exchange.¹⁵ Therefore, it is probable that pyridine at high temperature is singly dehydrogenated and is doubly adsorbed on the surface through the nitrogen and an ortho-carbon. The cross section of such a species is three by one-and-one-half in terms of the Pt(111) unit vectors and thus this adsorbed orientation of pyridine could give rise to the observed diffraction pattern. The decrease in the magnitude of the work function change is easily explained using this pyridine orientation since the nitrogen has a less favorable geometry for interaction with the surface.

Adsorption of these aromatic molecules on the Pt(100)-(5x1) surface led to the formation of disordered adsorbed layers. Little information can be extracted from the disordered diffraction patterns observed. Benzene adsorbed on the Pt(100)-(5x1) surface appears to go through reorientation with exposure as evidence by the corresponding change in the work function (Fig. 10).

One of the striking observations resulting from this study is the large difference in the ordering characteristics of the Pt(111) surface relative to the Pt(100)-(5×1) surface. Although these aromatic molecules may overlap several platinum atoms, it is clear that the interaction between the substrate and adsorbate is different for these two surfaces. The substrate periodicity is important; however, in these studies the fact that the (100) surface is reconstructed and changes from the (5×1) structure to a (1×1) structure on adsorption may also play a role in determining the interaction potential between substrate and adsorbate.

Xenon forms the same structure on several substrate surfaces.³ Thus it appears that the interaction between substrate and adsorbate is non-directional and does not depend strongly on either the electronic or geometric properties of the substrate. The aromatic molecules which were studied form surface structures that depend on the electronic and/or geometric properties of the substrate. Therefore the interaction potential between the metal surface and the aromatic adsorbates must depend on the relative positions of the adsorbed molecules and the substrate atoms, that is, the interaction appears to be localized and directional.

Acknowledgment. This work was supported by the U. S. Atomic Energy Commission.

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11. The underlying platinum unit cell is described by the matrix $\begin{vmatrix} 1\hat{a} & 0\hat{b} \\ 0\hat{a} & 1\hat{b} \end{vmatrix}$ or the row vectors $(1\hat{a}, 0\hat{b})$, $(0\hat{a}, 1\hat{b})$. The unit cell of the adsorbed structure $\begin{vmatrix} -2\hat{a} & 2\hat{b} \\ 4\hat{a} & 4\hat{b} \end{vmatrix}$ is described by the row vectors $(-2\hat{a}, 2\hat{b})$, $(4\hat{a}, 4\hat{b})$.
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