## Title
LOW ENERGY ELECTRON DIFFRACTION AND WORK FUNCTION CHANGE STUDIES OF THE ADSORPTION OF SUBSTITUTED AROMATIC MOLECULES ON THE (111) AND (100) CRYSTAL FACES OF PLATINUM

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# LOW ENERGY ELECTRON DIFFRACTION AND WORK FUNCTION CHANGE STUDIES OF THE ADSORPTION OF SUBSTITUTED AROMATIC MOLECULES ON THE (111) AND (100) CRYSTAL FACES OF PLATINUM

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## Abstract

The chemisorption of toluene, m-xylene, mesitylene, n-butylbenzene, t-butylbenzene, aniline, nitrobenzene and cyanobenzene were studied on the (111) and (100) crystal faces of platinum at low pressures ($10^{-9}$ to $10^{-7}$ torr) and at temperatures of 20° to 300°C by low energy electron diffraction and work function change measurements. After adsorption, reorientation of the molecules in the adsorbed layer is necessary to form the ordered structures. Molecules that have either higher rotational symmetry (mesitylene) or have only small size substituents on the benzene rings exhibit better ordering if the adsorption is carried out at low incident flux. The adsorbed layers are more ordered on the (111) crystal face than on the (100) crystal face of platinum. The work function changes upon adsorption range from -1.4 eV for nitrobenzene to -1.8 eV for aniline. Both the diffraction and work function change data indicate that, under the conditions of these experiments, all of the molecules chemisorb with their benzene ring parallel to the surface and interact with the metal surface primarily via the π-electrons in the benzene ring. The substituent groups play an important role in determining the ordering characteristics of the overlayers but do not markedly effect the strength of the chemical bond between the substrate and the adsorbate.

## Introduction

The interaction of organic molecules with metal surfaces is of primary importance in several areas of surface science. Adsorption of organic layers plays a large role in lubrication, in the adhesion of protective films, and in catalytic processes. The properties of adsorbed layers depend on the interaction between the adsorbed molecules and the metal. This paper reports the results of a study of the interaction of aromatic compounds with platinum single crystal surfaces. Low Energy Electron Diffraction (LEED) has been used to monitor the surface structures of the adsorbed layers on the Pt(111) and Pt(100)-(5x1) crystal surfaces. Work function changes (WFC, $\Delta\phi$) on adsorption have been used to determine the charge transfer occurring on adsorption. Both the charge transfer which occurs on adsorption and the structures formed have been used to obtain information about the nature of the interaction between the organic overlayer and the metal substrate.

Since there are a large number of organic molecules available for adsorption, the properties of the adsorbed molecules can be easily varied to facilitate exploration of the interaction between the adsorbed organic layer and the substrate. We have studied a selected group of aromatic compounds and systematically varied their geometry and chemical properties by changing substituents on the aromatic ring. Correlating variations in molecular structure and chemistry with variations in surface structure and interaction characteristics (as determined by LEED and WFC) for the molecules studied, will assist in predicting structures and interaction characteristics of other organic molecules which have not, or can not, be studied by these techniques. We have studied the properties of adsorbed layers of a series of substituted aromatic compounds using methyl groups in increasing numbers to replace the hydrogen atoms in the benzene rings [toluene ($C_6H_5$-$CH_3$), meta-xylene ($C_6H_4$-$(CH_3)_2$), and mesitylene ($C_6H_3$-$(CH_3)_3$)]. We have also studied a series of mono-substituted aromatic molecules with aliphatic side chains of increasing length and branching [toluene ($C_6H_5$-$CH_3$), n-butylbenzene ($C_6H_5$-$C_4H_9$) and t-butylbenzene ($C_6H_5$-$C_4H_9$)]. ← Finally a series of mono-substituted aromatic molecules with substituents of different electronegativity [toluene ($C_6H_5$-$CH_3$), aniline ($C_6H_5$-$NH_2$), nitrobenzene ($C_6H_5$-$NO_2$) and cyanobenzene ($C_6H_5$-CN)] were studied. The experiments were carried out in the temperature range of 20° to 300°C and at pressures of the organic vapors in the range of $10^{-9}$ to $10^{-7}$ torr.

We have found that ordering of the adsorbed layer requires reorientation of the molecules on the surface. Ordering is easier for molecules with higher rotational symmetry. Order is also more prevalent on substrates with higher rotational multiplicity. Under the experimental conditions used, all of the molecules studied chemisorb on both the (111) and (100) surfaces of platinum with their aromatic rings parallel to the substrate surface. The adsorbates interact with the metal surface primarily via the formation of a $\pi$ bond between their aromatic $\pi$-electron and the electron deficient metal surface. This type of interaction results in the large work function changes observed.

## Experimental

The experimental procedures used have been described in detail elsewhere.[1,2] Summarizing briefly, a modified Varian LEED system capable of obtaining a typical ambient pressure of 2 x $10^{-9}$ torr was used. All adsorption data was taken at 25°-40°C unless otherwise noted. Diffraction data was taken using a 4-grid Varian post-acceleration LEED apparatus. Work function changes (WFC, $\Delta\phi$) caused by adsorption were measured by the retarding field method using the LEED gun as the electron beam source.[1,2] The retarding potentials were used as an internal voltage standard for the work function change measurements.

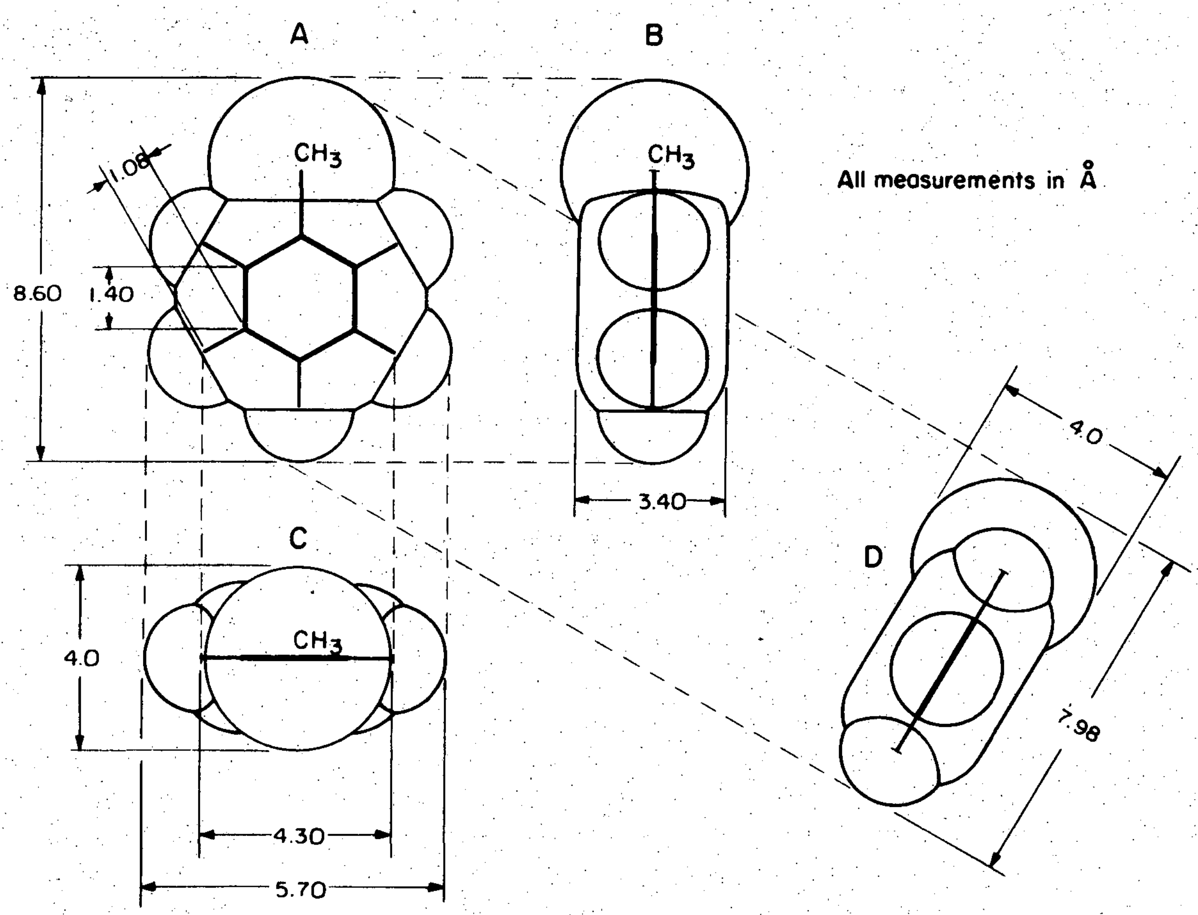
Prior to each adsorption experiment, the platinum samples were treated with oxygen at pressures of 1 to 3 x $10^{-5}$ torr for 60 minutes at 1000°C to remove the carbon impurities present on the surface. After terminating the gas flow, the system was pumped down to a pressure of 1 x $10^{-8}$ torr using the large ion pump and titanium sublimation pump; the electron guns were then degassed and warmed up. The single crystal samples remain at 1000°C for a period of 30-45 minutes in vacuum. 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 mandatory. Following gun stabilization, the crystals were heated to 1000°C for 5 minutes. The crystal surfaces produced in this manner were clean, within the limits detectable by Auger electron spectroscopy, and showed the characteristic Pt(111)-(1x1) and Pt(100)-(5x1) diffraction patterns. The crystals were then allowed to cool to 25-40°C in a background pressure of $1 \times 10^{-9}$ torr. The cooling took approximately 20 to 40 minutes. The organic vapor flux was introduced from a capillary tube approximately 5 mm from the sample surface. The flux at the sample surface is approximately 6 times the background pressure quoted on all figures since the system is operated as a steady state flow system during the adsorption experiment.

The adsorbates used were specified as better than 99% pure by the manufacturer and used without further purification. They were degassed by alternate freezing and thawing on an auxilary glass-teflon vacuum system.

The geometry of the adsorbate molecules studied is shown in Figures 1-8.[3,4] The van der Waals radius used for hydrogen is 1.2 Å, and for the methyl group 2.0 Å.[4] The thickness of the aromatic ring system is taken as 3.4 Å.[4] The molecules are shown in various projections since several adsorption geometries are possible in some cases.

A series of measurements were made to determine the size of the adsorbate induced unit cell. Uncertainties of ±5% are typical because of the diffuse diffraction features which occur throughout this work. Average values are quoted throughout.

The LEED results quoted have been observed on three different sets of single crystal samples for toluene, t-butylbenzene, aniline, nitrobenzene,



Toluene

XBL 737-6378

Figure 1 The structure of toluene with van der Waals radii shown.

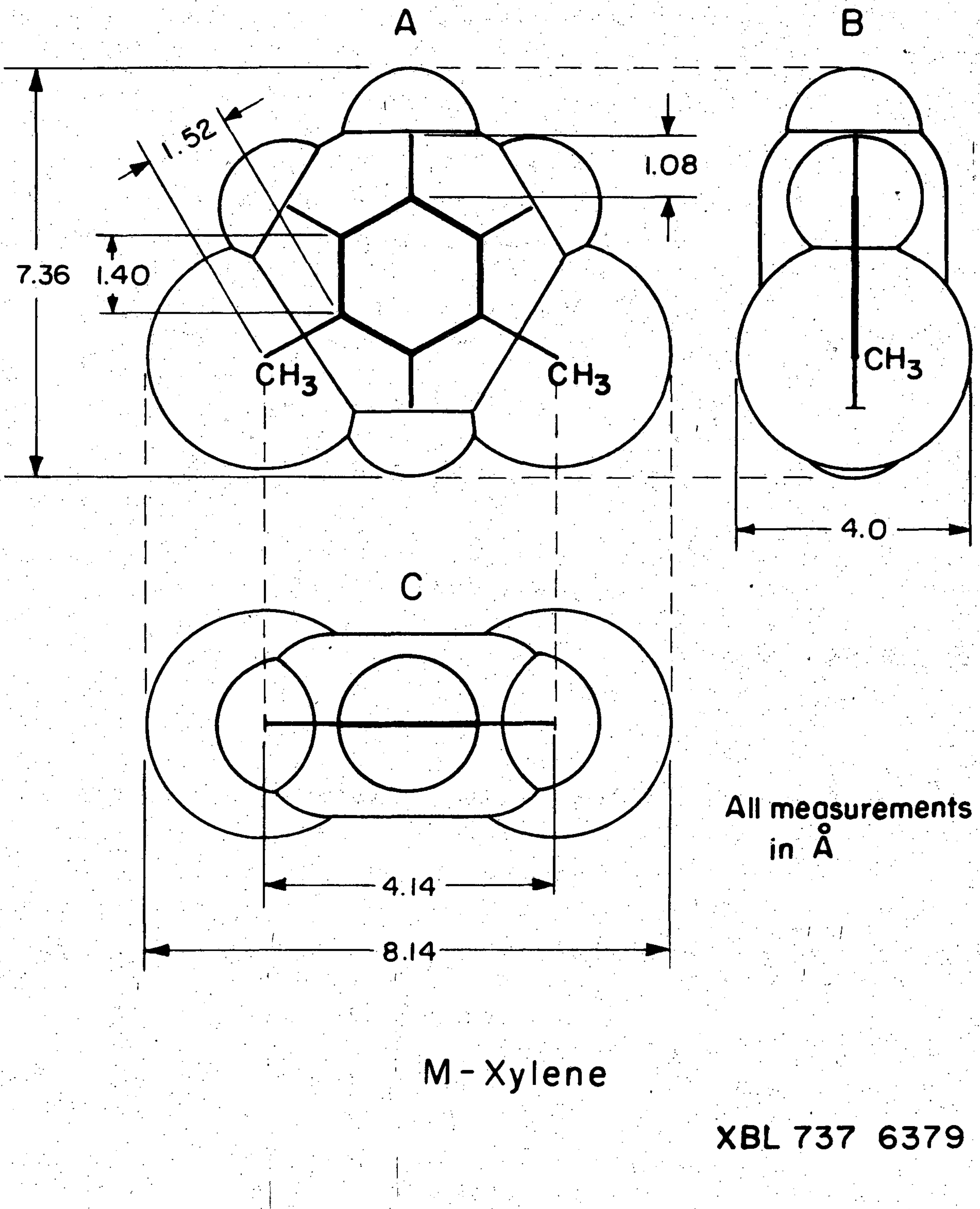
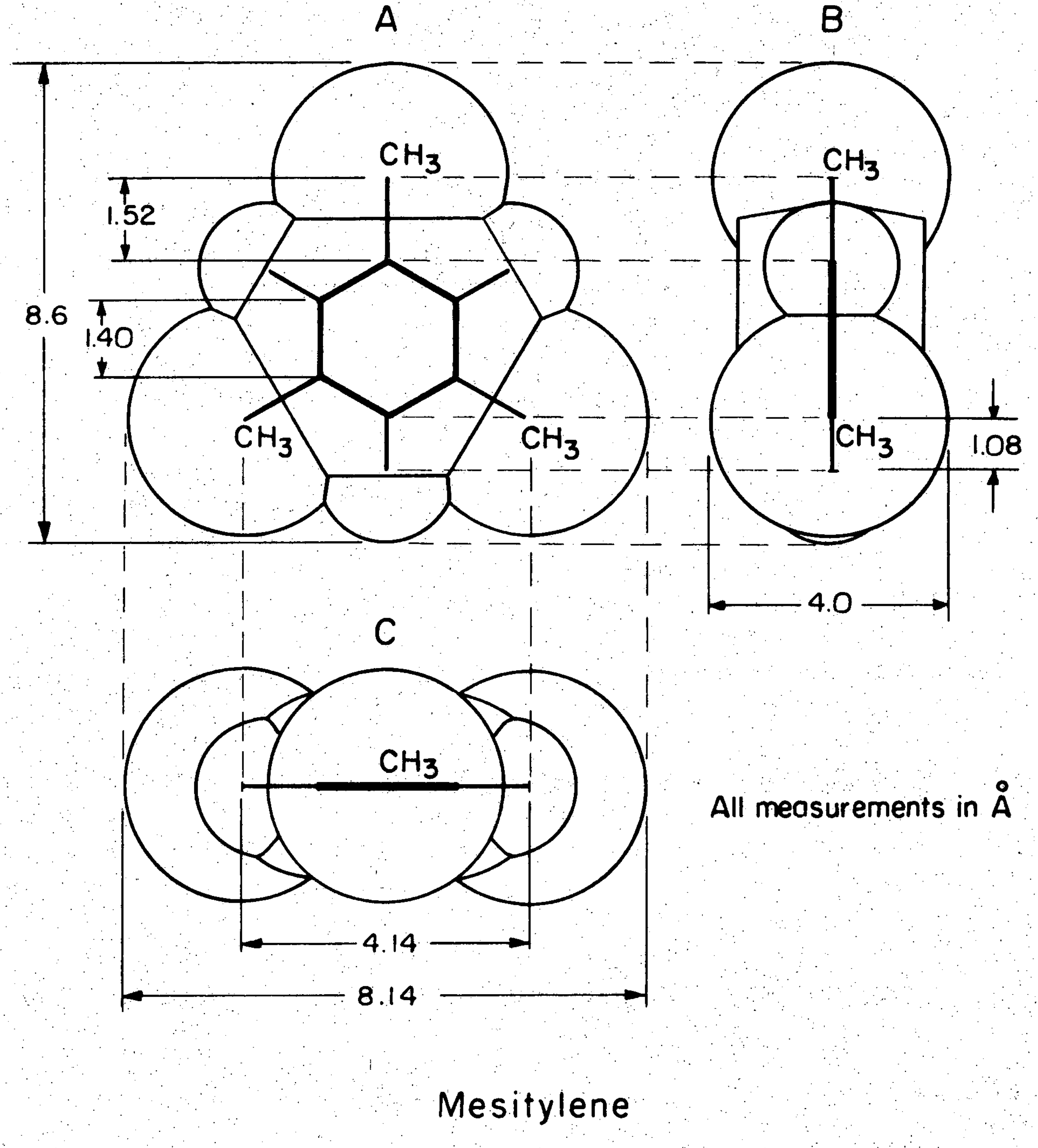
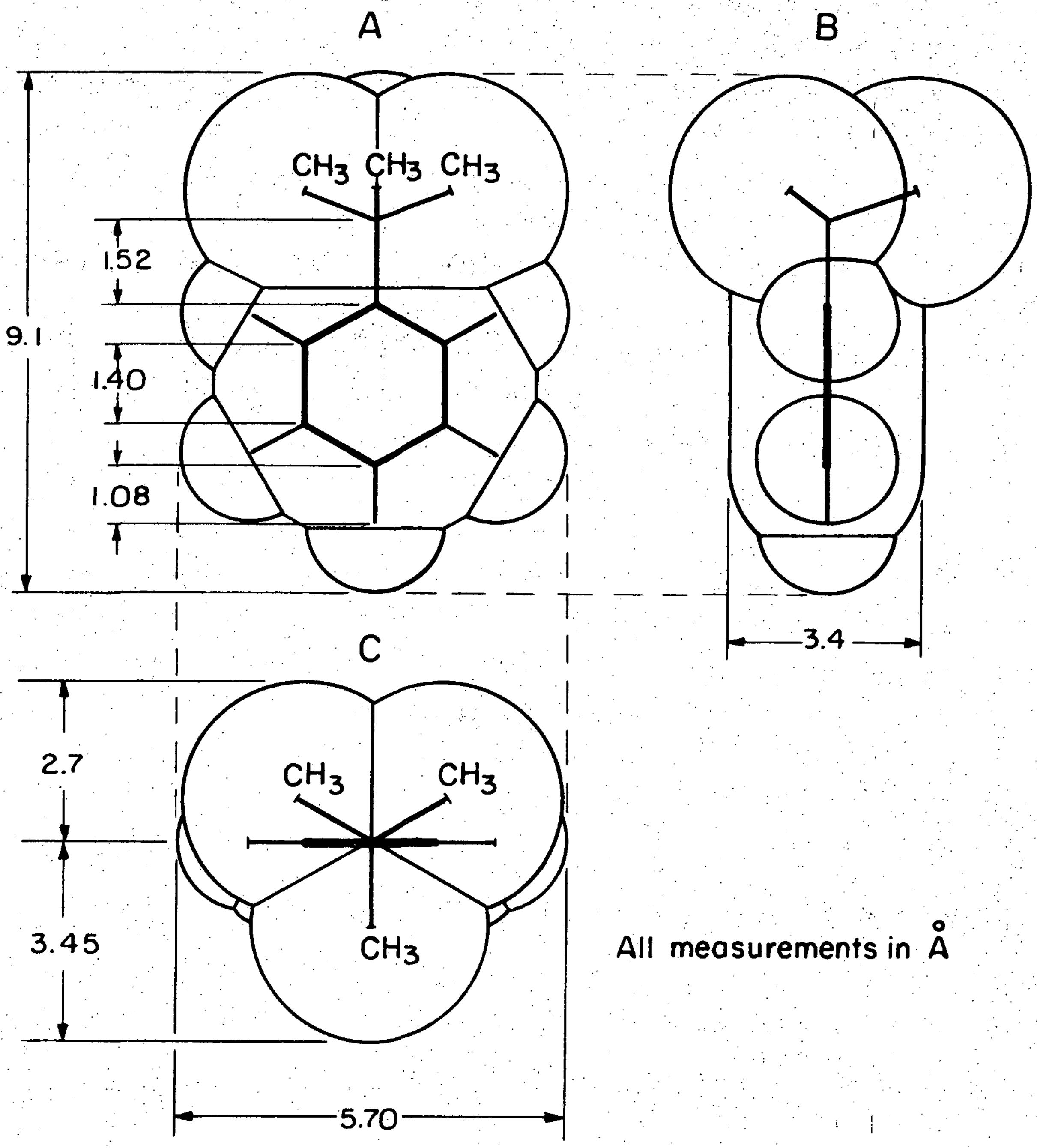


Figure 2 The structure of m-xylene with van der Waals radii shown.



XBL 737-6380

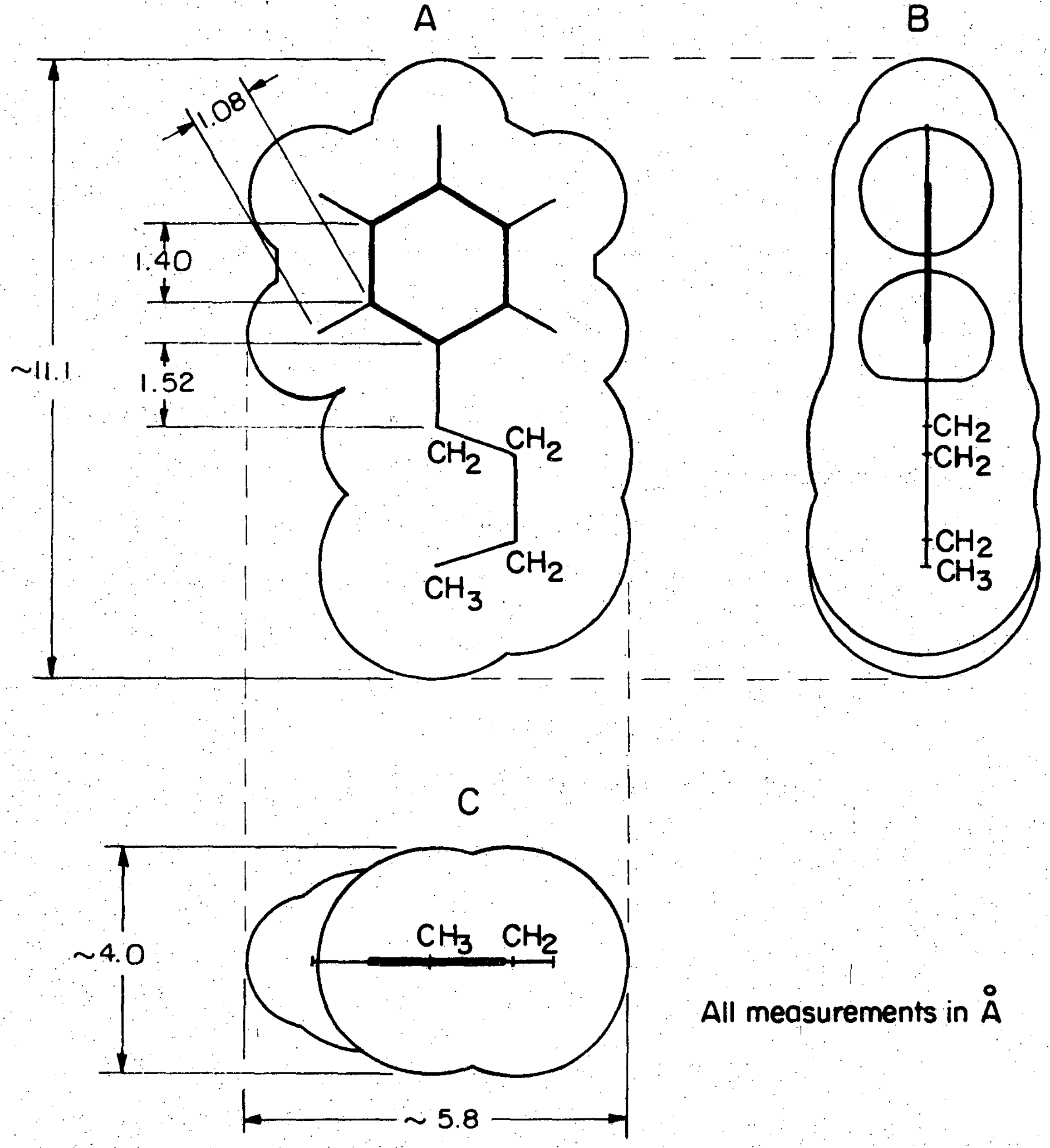
Figure 3 The structure of mesitylene with van der Waals radii shown.



T- Butylbenzene

XBL 737-6381

Figure 4 The structure of t-butylbenzene with van der Waals radii shown.

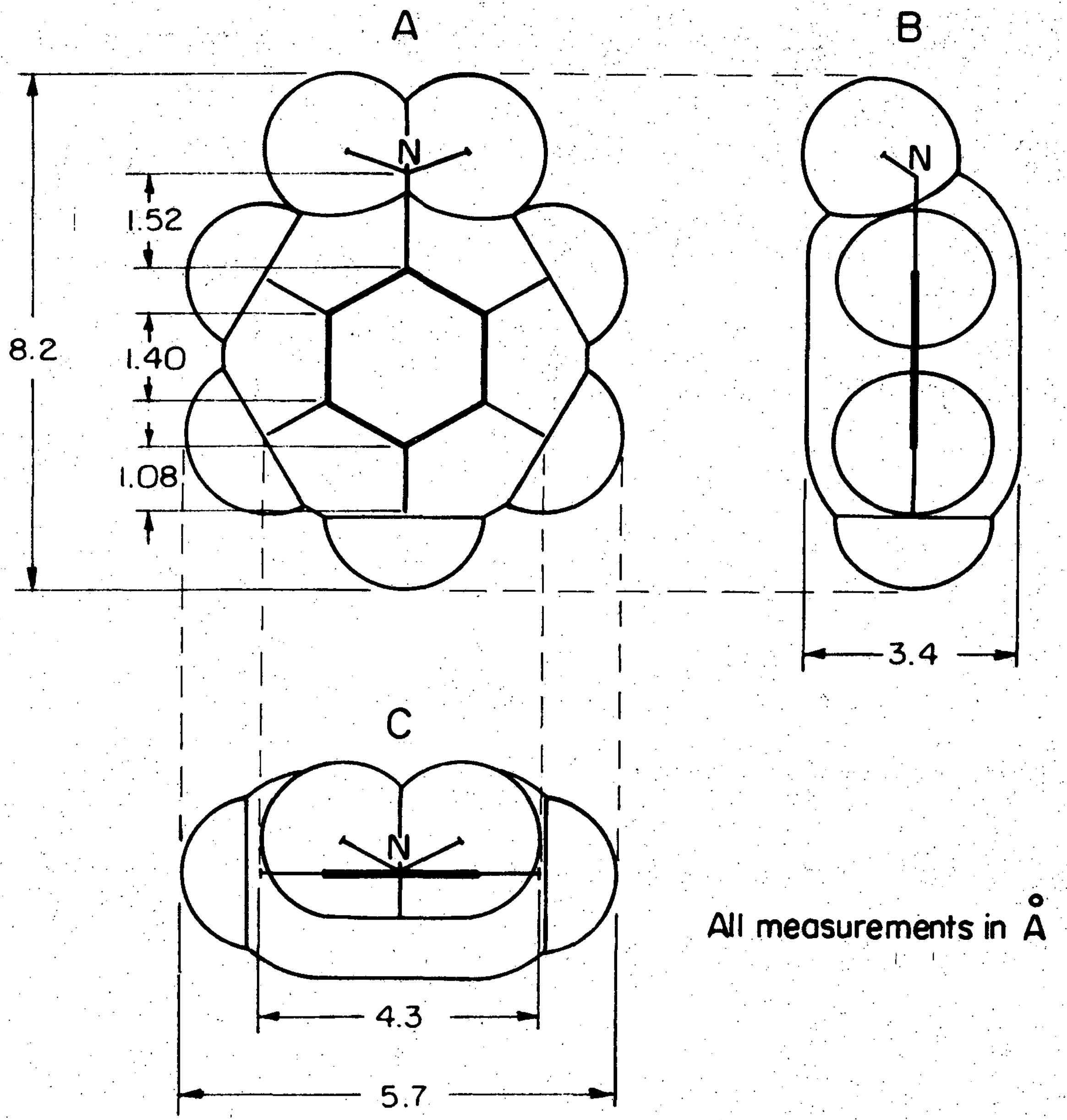


N - Butylbenzene

(one of the possible flat configurations)

XBL 737- 6382

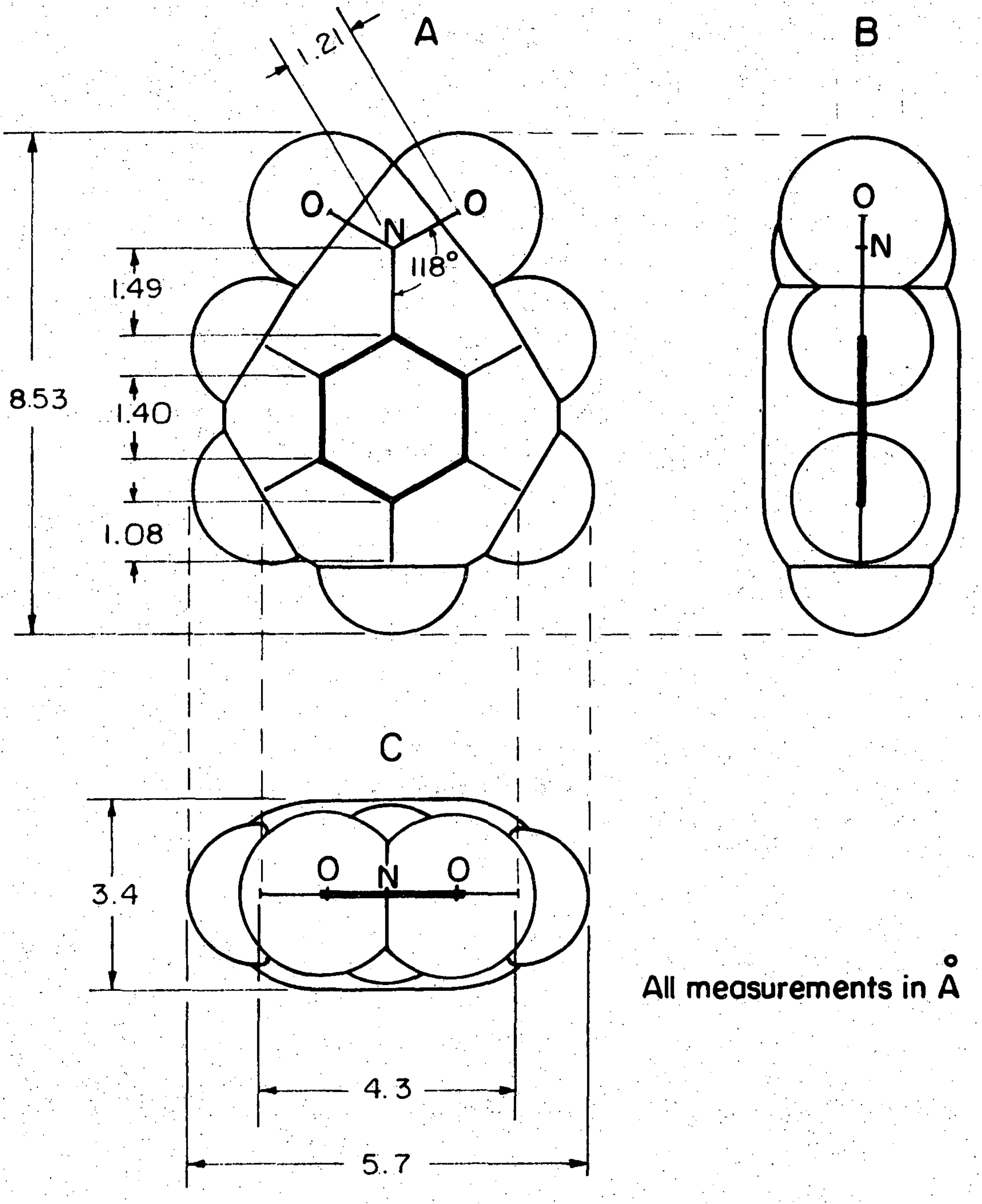
Figure 5 The structure of n-butylbenzene with van der Waals radii shown.



Aniline

XBL737-6383

Figure 6    The structure of aniline with van der Waals radii shown.



Nitrobenzene

XBL 737-6384

Figure 7 The structure of nitrobenzene with van der Waals radii shown.

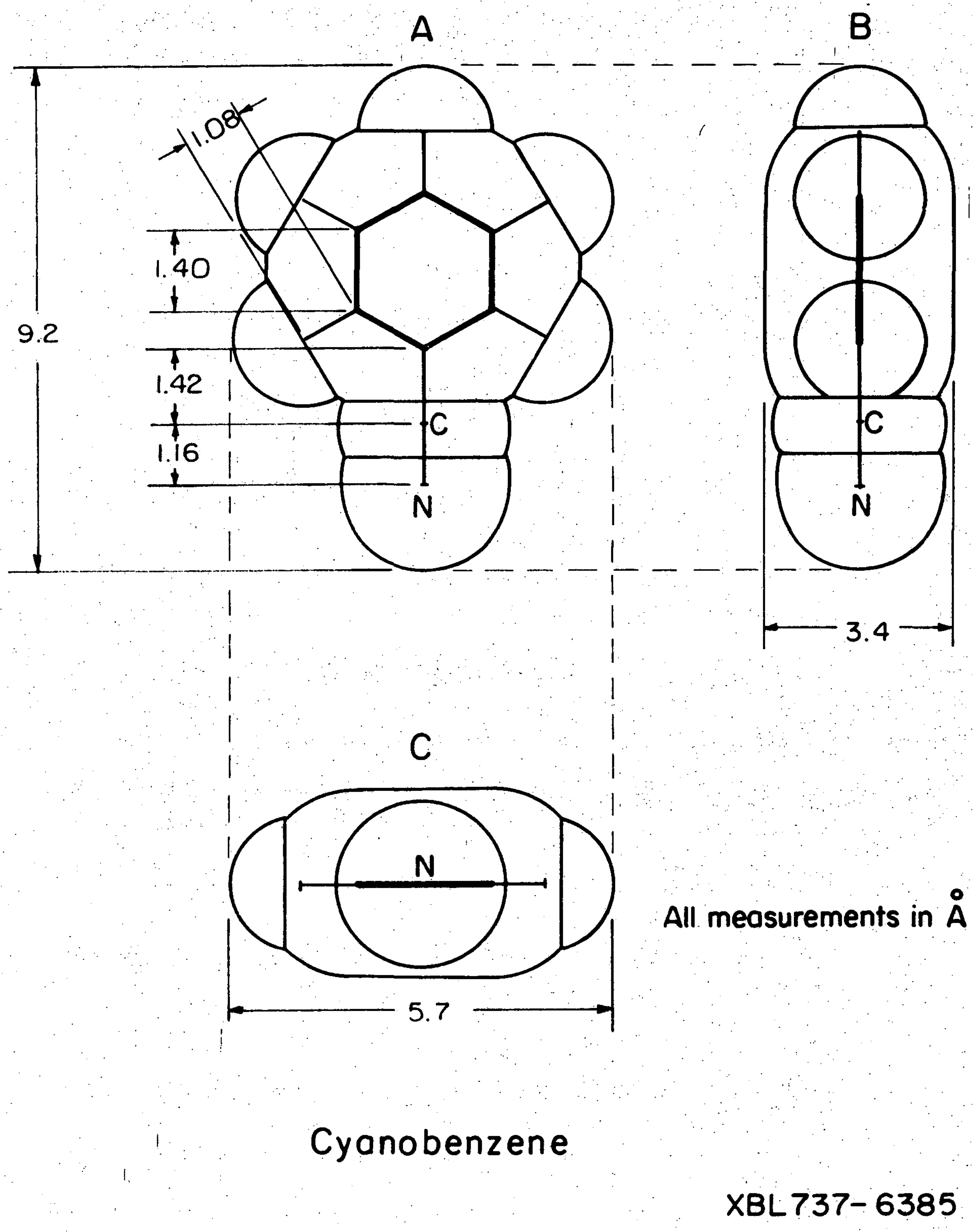


Figure 8 The structure of cyanobenzene with van der Waals radii shown.

and cyanobenzene. The WFC results for the above mentioned set of compounds were taken on two sets of single crystal samples. No significant variation has been observed between different single crystal samples if comparisons are made between adsorption experiments carried out under similar conditions of pressure and temperature.

The LEED patterns observed vary markedly with contamination of the single crystal surfaces. The LEED results were difficult to reproduce without titanium sublimation pumping because of rapid carbon monoxide contamination of the platinum surface at room temperature. If the surfaces are not heated sufficiently in vacuum to remove adsorbed oxygen (from cleaning) the results are also not reproducible. Even slight carbon contamination of the surface leads to irreproducible results. Slight misalignment of the low index surface, resulting in high density of atomic steps, results in a marked change in the adsorption characteristic.[5] During this work we installed a (111) crystal which was misaligned by 2°. The LEED patterns resulting from adsorption on this crystal as well as the WFC observed on adsorption were markedly altered.

Preliminary experiments have indicated that adsorption at higher pressures ($10^{-7}$ torr) may cause marked changes in the interaction between substrate and adsorbate because of chemical reactions in the adsorbed layer. Both diffraction patterns and WFC change significantly with increases in pressure.

## Results

Toluene, m-xylene, mesitylene, t-butylbenzene, n-butylbenzene, aniline, nitrobenzene and cyanobenzene adsorb on both the Pt(111) and Pt(100)-(5x1) surfaces. The diffraction features or surface structures which were detected and the work function changes (WFC) that accompany adsorption are listed in Table I. The structures formed on adsorption exhibit better order on the Pt(111) surface than on the Pt(100)-(5x1) surface. In general, the WFC measured depends on the initial incident vapor flux. All adsorbates studied act as electron donors to the metal.

Toluene adsorption: Toluene adsorbed on the Pt(111) surface causes the formation of a poorly ordered adsorbed layer with streaks at 1/3 order with respect to the first order platinum features. The diffraction pattern observed is shown in Figures 9a and 9b. The work function change on adsorption is approximately -1.7V (Figure 10); however, the WFC depends on the initial incident vapor flux. If the poorly ordered adsorbed layer is heated to 150°C, ordering is greatly improved and the Pt(111)-(4x2)-toluene structure forms. The diffraction patterns observed are shown in Figures 9c and 9d. The WFC does not appear to be effected by reordering of the adsorbate layer( as shown in Figure 11).

Toluene adsorbed on the Pt(100)-(5x1) surface causes the appearance of 1/3 order streaks in the diffraction pattern, while the characteristic (5x1) diffraction features remain. The diffraction pattern observed is shown in Figure 12. The diffraction pattern indicates the presence of two domains of the surface structure at right angles to each other.

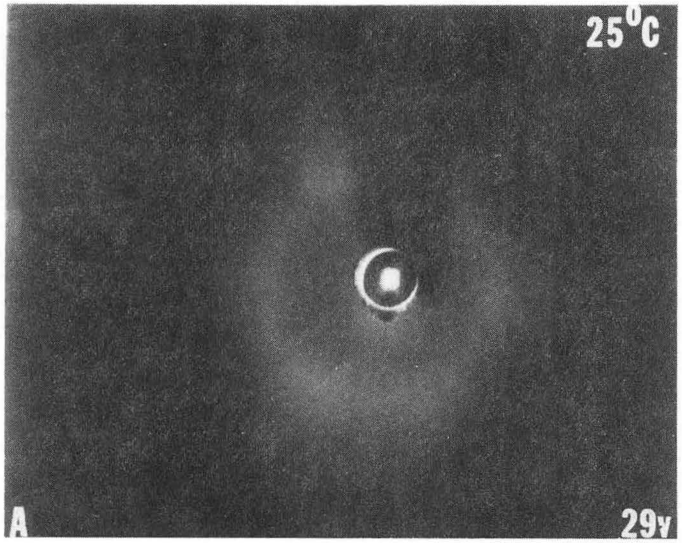
Table I

The maximum work function change and structural information for the adsorption of toluene, m-xylene, mesitylene, t-butylbenzene, n-butylbenzene, aniline, nitrobenzene, cyanobenzene, and graphite on the Pt(111) and Pt(100)-(5x1) surfaces at 25°C.

| | | Pt(111)* | | Pt(100)-(5x1) | | |
|---|---|---|---|---|---|---|
| | T(C) | Work Function Change ($\Delta\phi$) | Adsorbate Diffraction Features or Structure | Work Function Change ($\Delta\phi$) | Substrate Structure After Adsorption | Adsorbate Diffraction Features or Structure |
| Toluene | 20° | -1.7V | streaks at 1/3 order | -1.55V | (5x1) | streaks at 1/3 order |
| | 150° | | (4x2) | | (1x1) | high background |
| M-xylene | 20° | -1.8V | streaks at 1/2.6 order | -1.65V | (5x1) | streaks at 1/3 order |
| Mesitylene | 20° | -1.7V | streaks at 1/3.4 order | -1.7V | (5x1) | streaks at 1/3 order |
| T-butylbenzene | 20° | -1.7V | disordered | -1.75V | (1x1) | disordered |
| N-butylbenzene | 20° | -1.5V | disordered | -1.5V | (1x1) | disordered |
| Aniline | 20° | -1.8V | streaks at 1/3 order | -1.75V | (1x1) | disordered |
| Nitrobenzene | 20° | -1.5V | 1/3 order features (structure and WFC sensitive to electron bombardment) | -1.4V | (1x1) | disordered |
| Cyanobenzene | 20° | -1.6V | 1/3 order features | -1.5V | (5x1) | disordered |
| Graphitic overlayer | 900° | -1.1V | ringlike diffraction features | -1.1V | (1x1) | ringlike diffraction features |

*The structure of the Pt(111) substrate is always (1x1).

(a) The diffraction pattern resulting from toluene adsorption on the Pt(111) surface.



(c) The diffraction pattern resulting from 160°C heat treatment of the structure that exhibits the diffraction pattern shown in A.

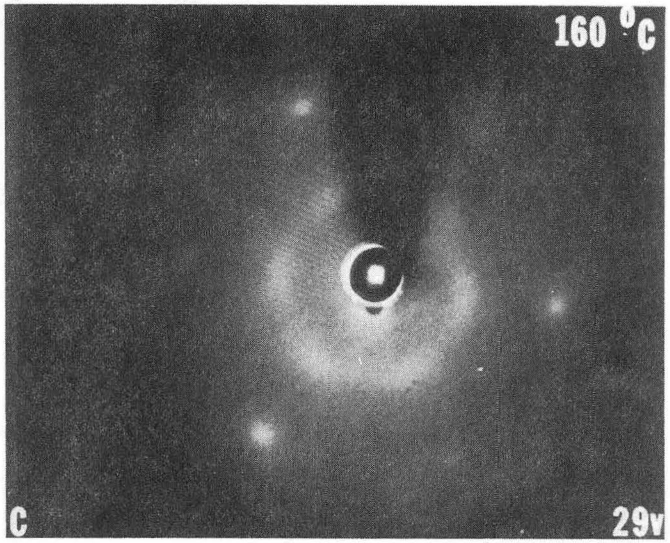
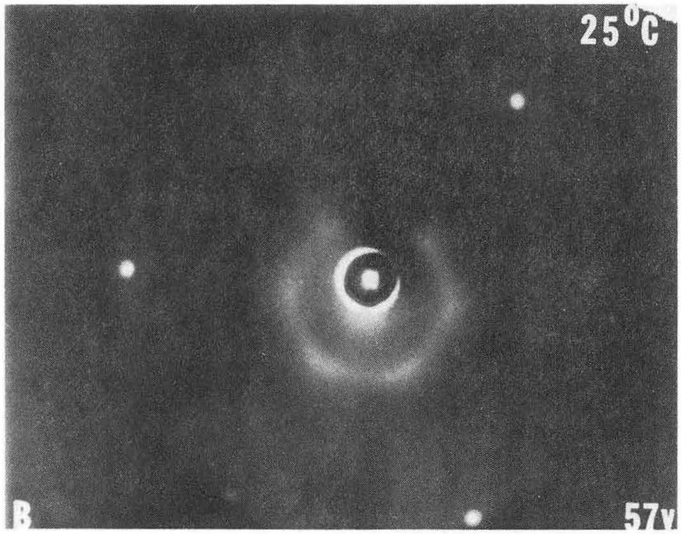
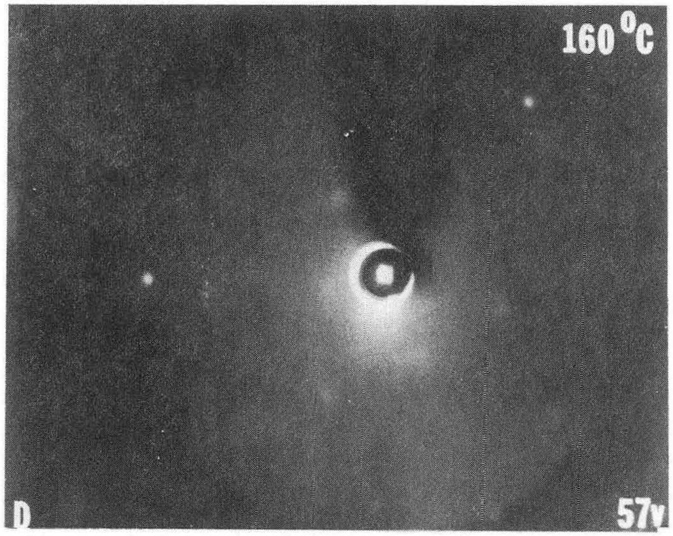


Figure 9

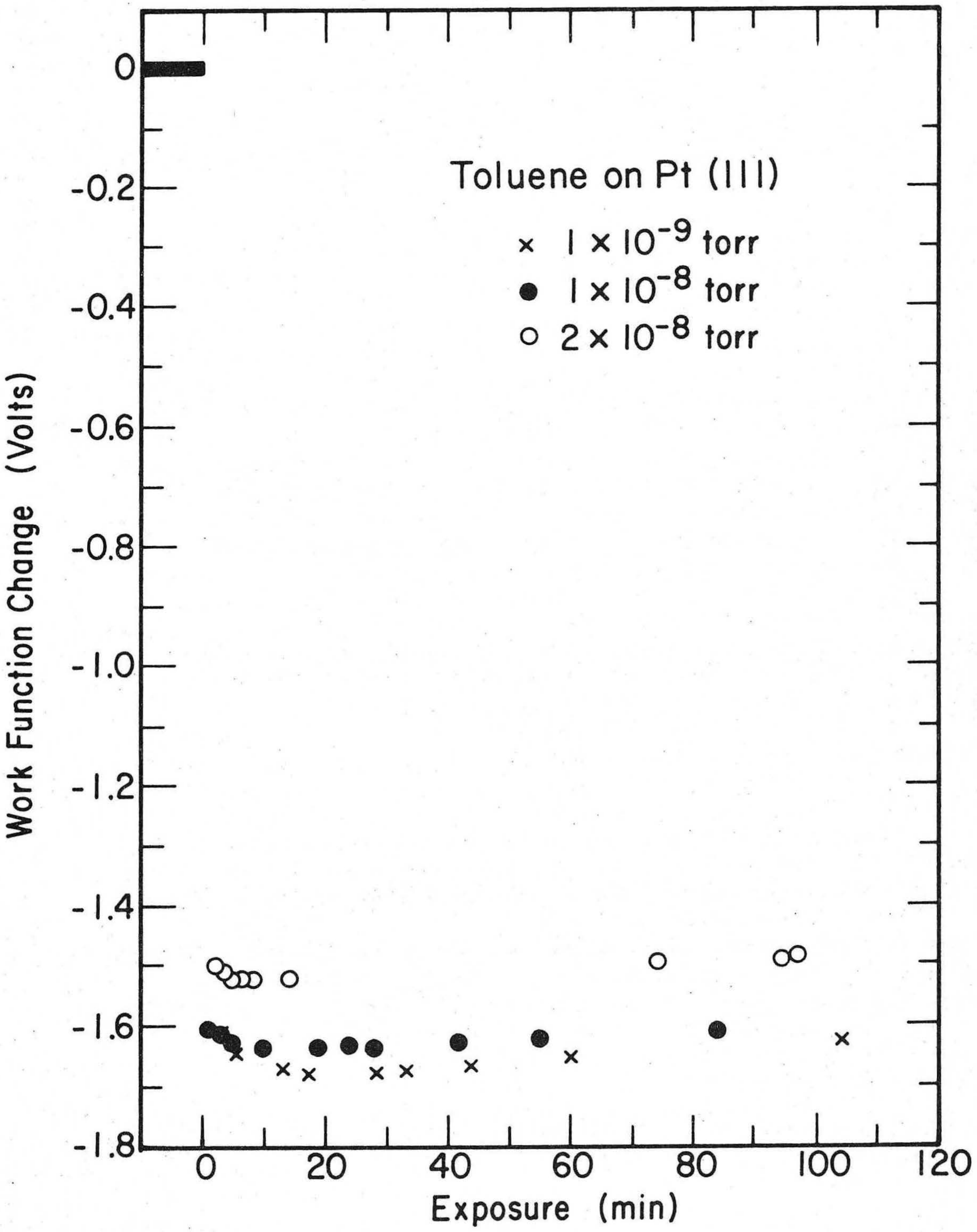


(b) The diffraction pattern resulting from toluene adsorption on the Pt(111) surface. The first order Pt diffraction features are also visible.



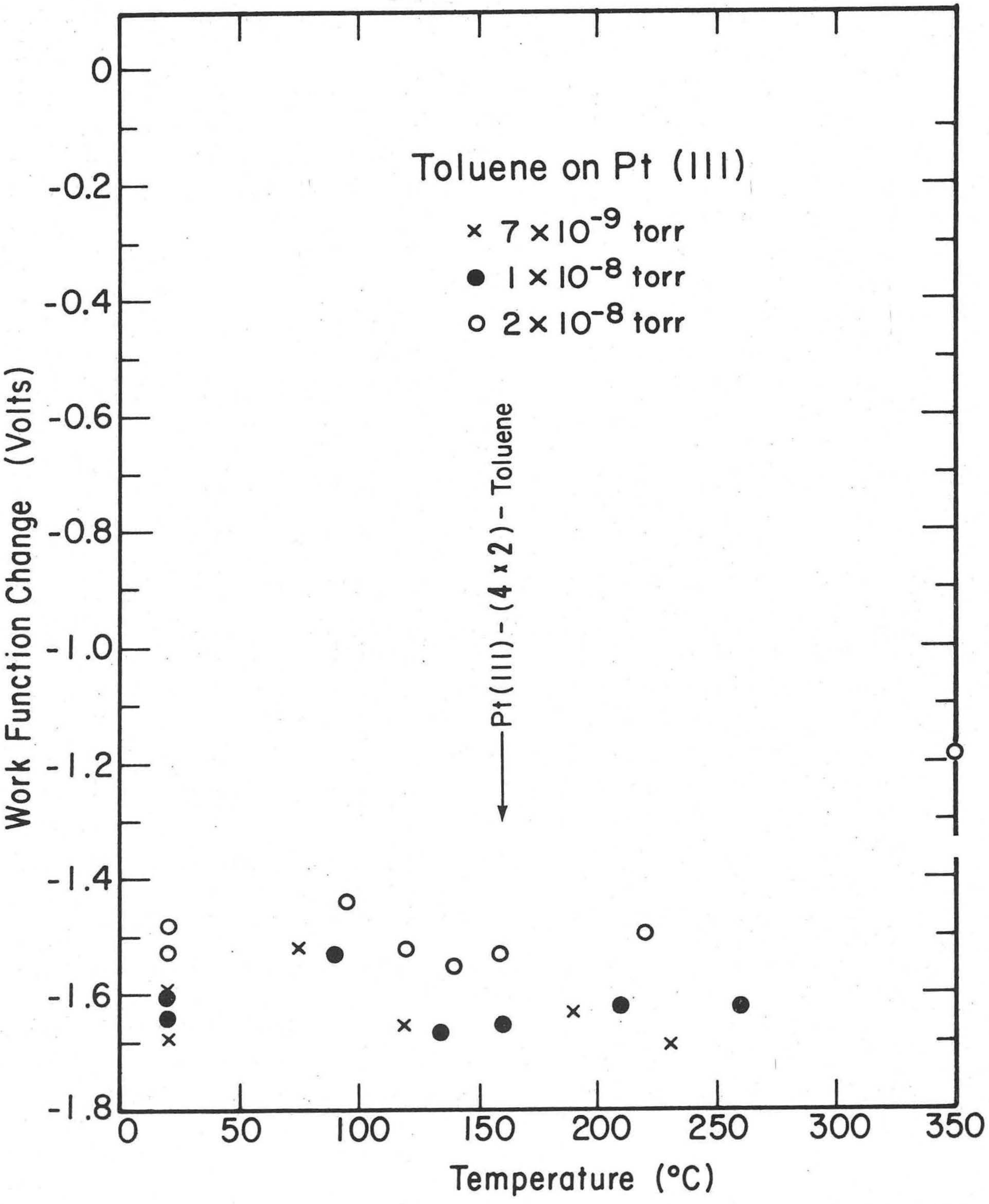
(d) The diffraction pattern resulting from 160°C heat treatment of the surface with adsorbed toluene. The first order Pt diffraction features are also visible.

XBB 732-680



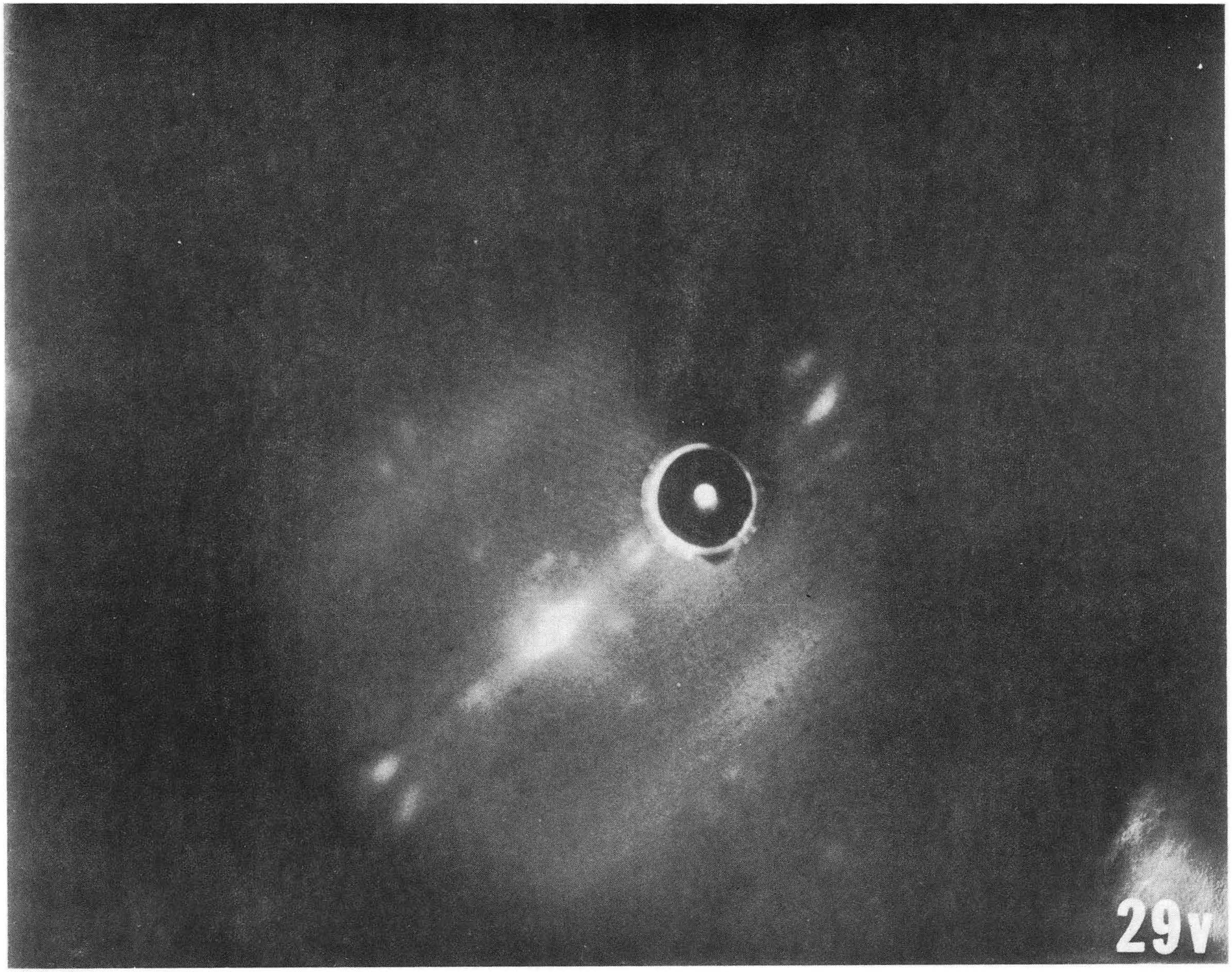
XBL732-5757

Figure 10 Work function change as a function of time during toluene adsorption on the Pt(111) surface. The indicated pressure should be multiplied by 6 to give the effective pressure at the surface.



XBL 732-5763

Figure 11 Work function change as a function of surface temperature for toluene adsorption on the Pt(111) surface. The pressure should be multiplied by 6 to give the effective pressure at the surface.



XBB 732-675

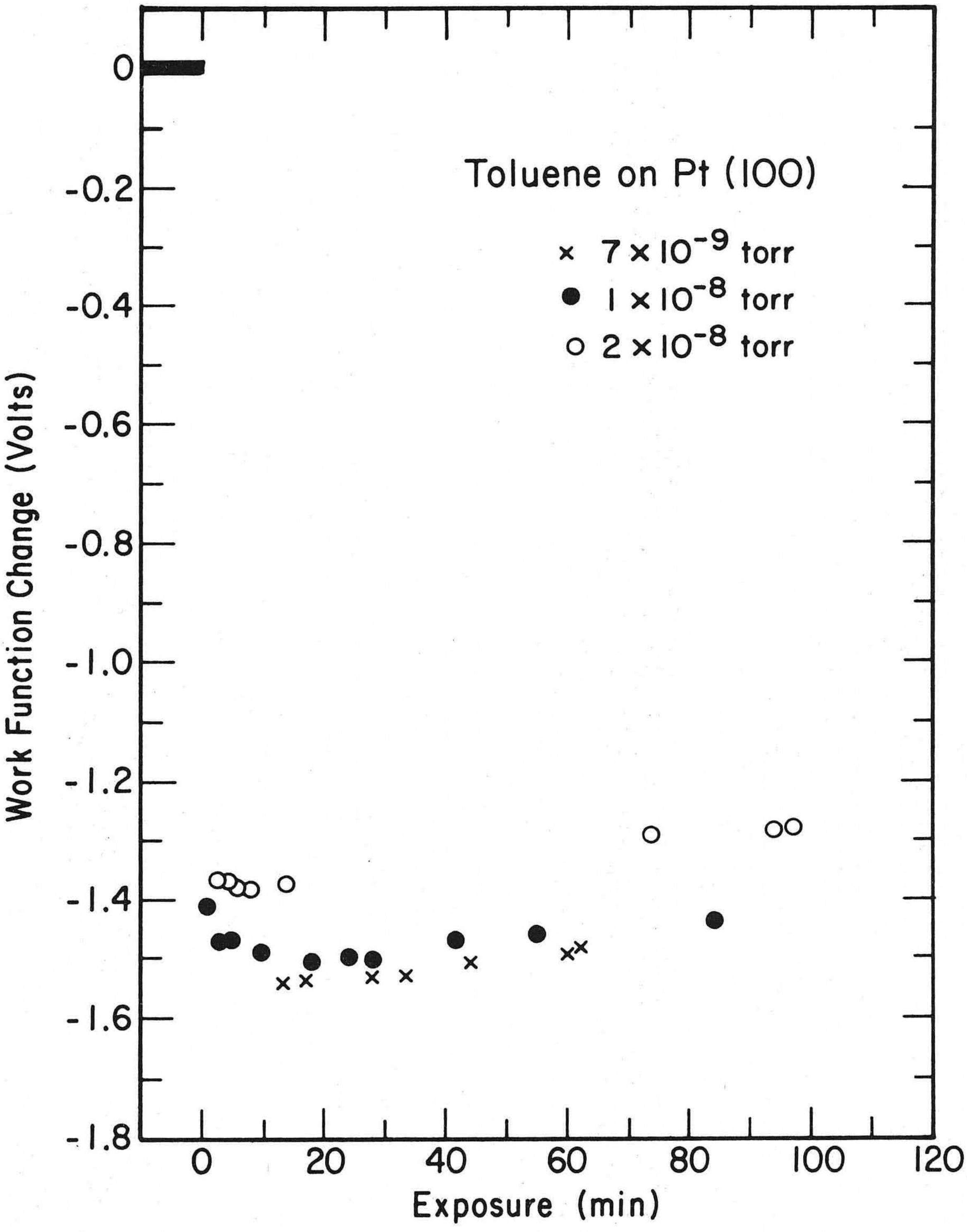
Figure 12 The diffraction pattern resulting from toluene adsorption on the Pt(100)-(5x1) surface.

Observations have been made on a single domain. The domains of the adsorbed layer are coincident with domains of the (5x1) structure. When viewing a single domain, the 1/3 order streaks are always parallel with the direction of the 1/5 order diffraction features.

On heating to 150°C during continued exposure to the vapor flux, the diffraction pattern indicates the formation of a poorly ordered (1x1) structure, and both the 1/3 order streaks and (5x1) diffraction features disappear. The WFC on adsorption is approximately -1.55V (Figure 13); however, the magnitude of the WFC depends on the initial incident flux. During heating in flux, the WFC varies only slightly (Figure 14).

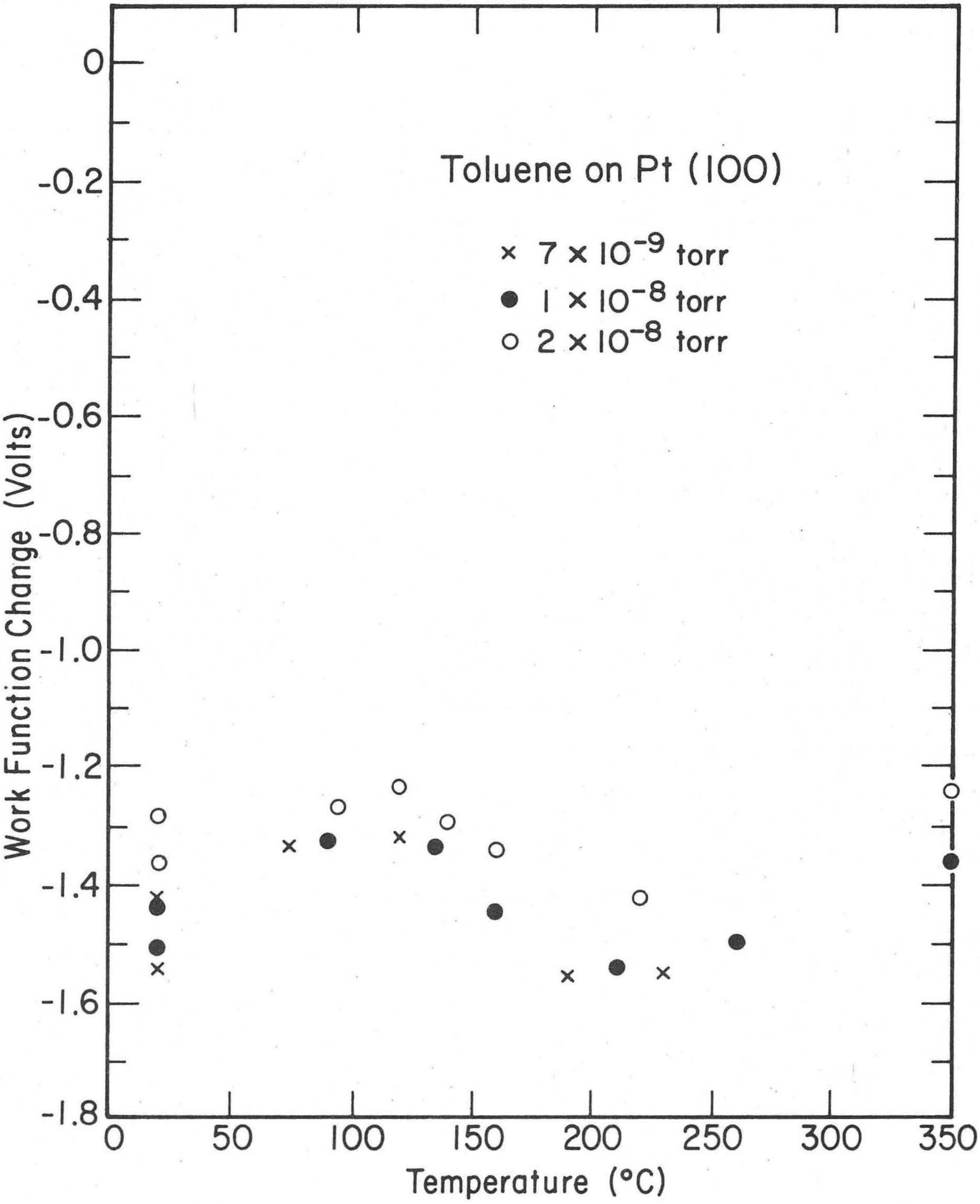
<u>M-xylene adsorption</u>: Meta-xylene, on adsorption on the Pt(111) surface, causes the formation of a poorly ordered surface structure. This is indicated by the poorly ordered diffraction pattern which exhibits streaks at 1/2.6 of the distance from the first order platinum diffraction beams to the (00) beam (Figure 15a). The WFC on adsorption is approximately -1.8V (Figure 16); and depends on the initial incident vapor flux.

M-xylene adsorbed on the Pt(100)-(5x1) surface causes the appearance of 1/3 order streaks while the 1/5 order diffraction features characteristic of the (5x1) structure remain (Figure 15b). The diffraction patterns that result from m-xylene and toluene adsorption are the same. The domains of the adsorbed structure are again parallel to the domains of the (5x1) structure. The WFC on adsorption is approximately -1.65V (Figure 17).



XBL732-5756

Figure 13 Work function change as a function of time during toluene adsorption on the Pt(100)-(5x1) surface. The pressure should be multiplied by 6 to give the effective pressure at the surface.

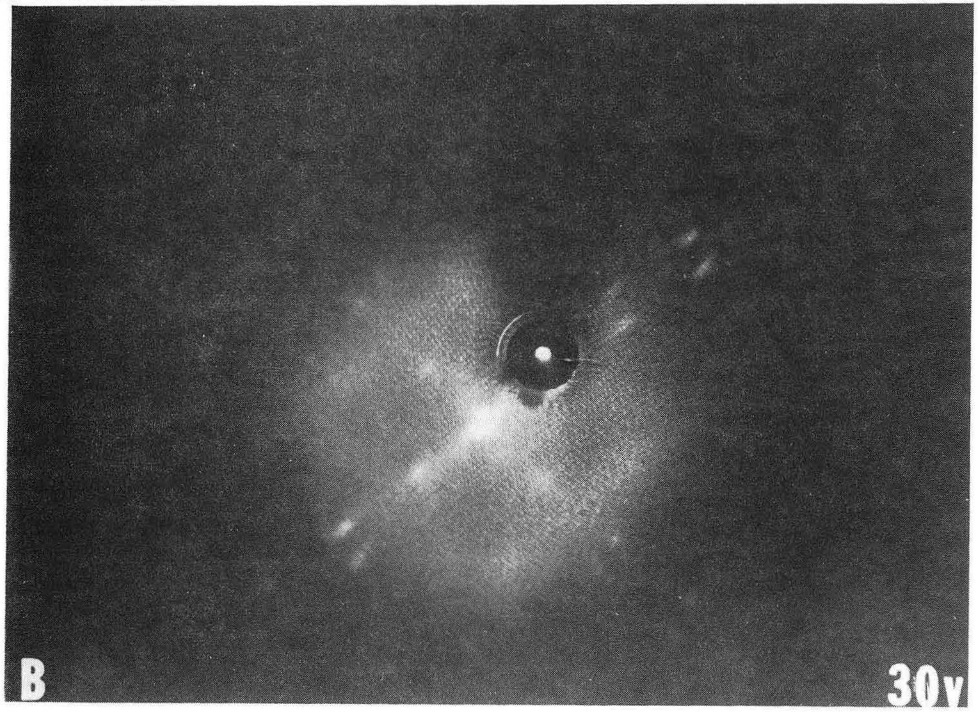


XBL 732-5762

Figure 14 Work function change as a function of temperature for toluene on the Pt(100)-(5x1) surface. The pressure should be multiplied by 6 to give the effective pressure at the surface.

Figure 15

(a) The diffraction pattern resulting from m-xylene adsorption on the Pt(111) surface showing the first order Pt diffraction features.



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(b) The diffraction pattern resulting from m-xylene adsorption on the Pt(100)-(5x1) surface.

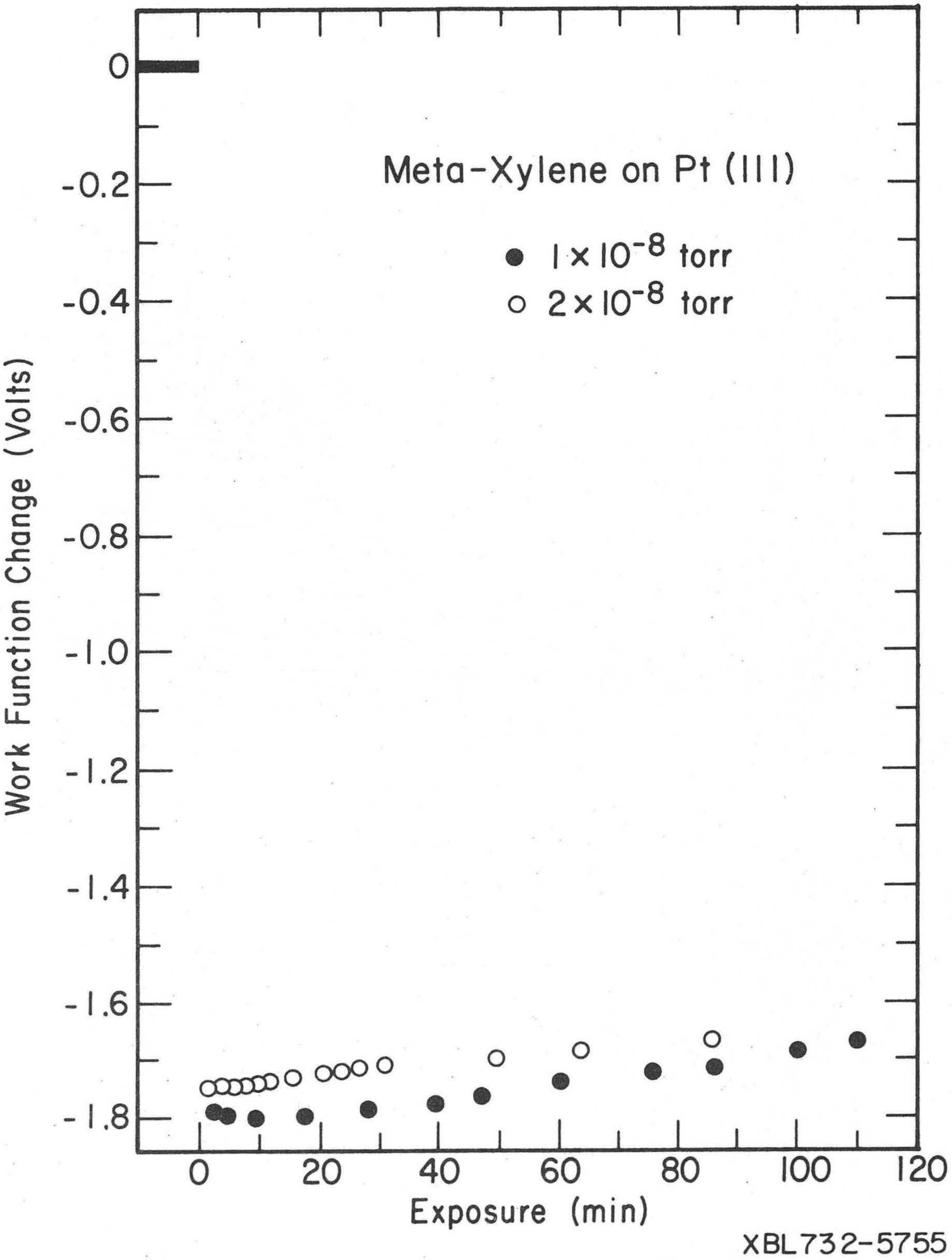
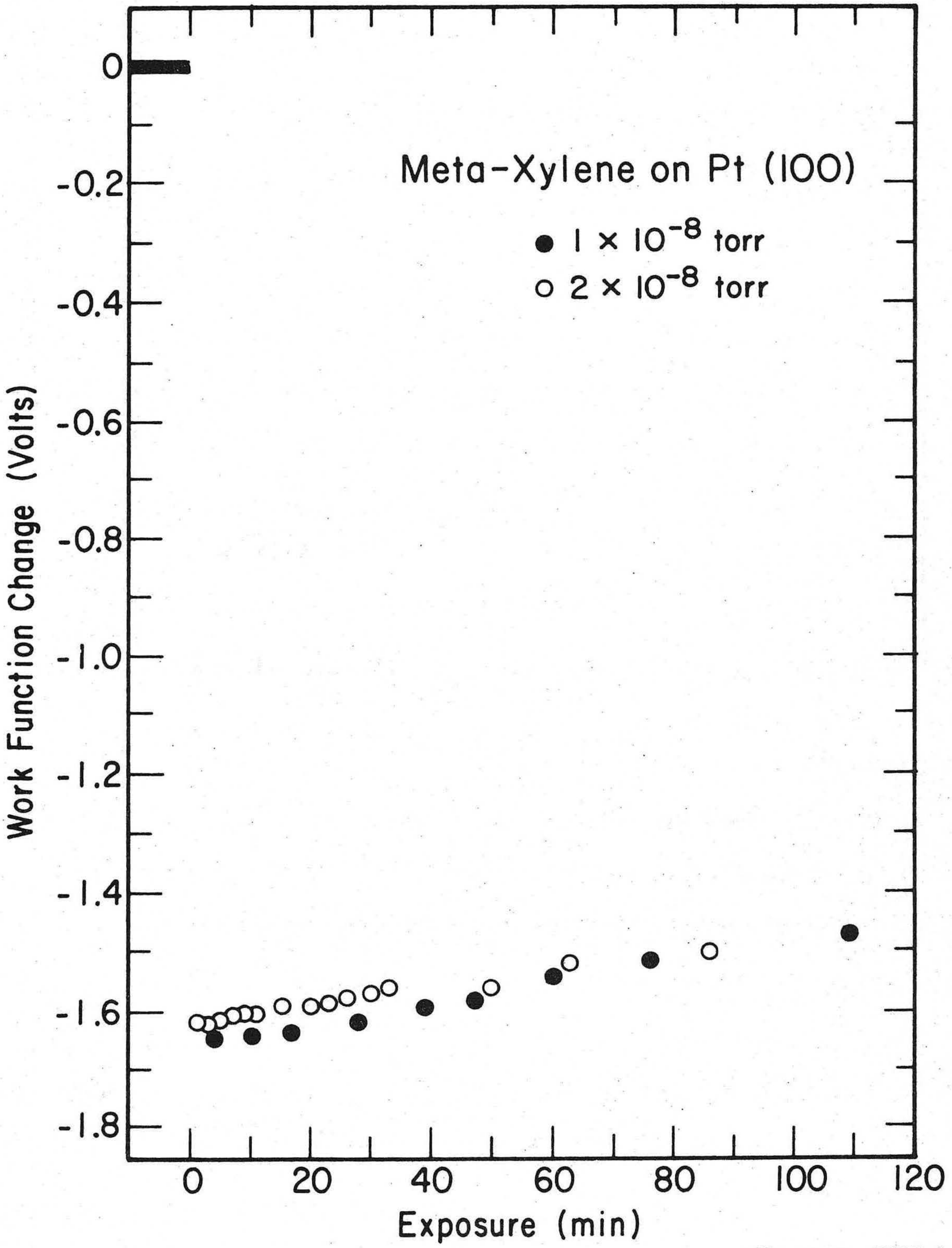


Figure 16 Work function change as a function of time for m-xylene adsorption on the Pt(111) surface. The pressure should be multiplied by 6 to give the effective pressure at the surface.



XBL732-5754

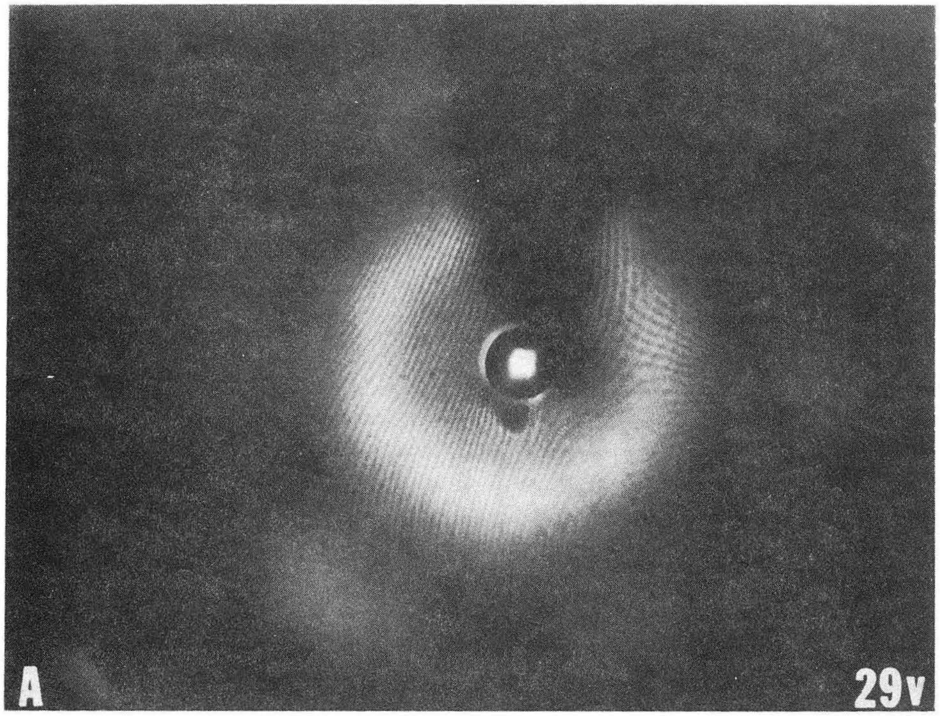
Figure 17 Work function change as a function of time during m-xylene adsorption on the Pt(100)-(5x1) surface. The pressure should be multiplied by 6 to give the effective surface pressure.

Mesitylene adsorption: Mesitylene adsorbed on the Pt(111) surface causes the formation of a poorly ordered adsorbed layer as indicated by the diffraction features which exhibit streaks at 1/3.4 order with respect to the Pt first order diffraction features. The second order streaks at 2/3.4 order are also visible. The diffraction pattern observed is shown in Figure 18. The WFC on adsorption is approximately -1.7V (Figure 19; however, the WFC and the degree of order of the surface structure depend on the initial incident vapor flux. At high initial fluxes (~$4 \times 10^{-7}$ torr) the layer is disordered and has a small WFC on adsorption.

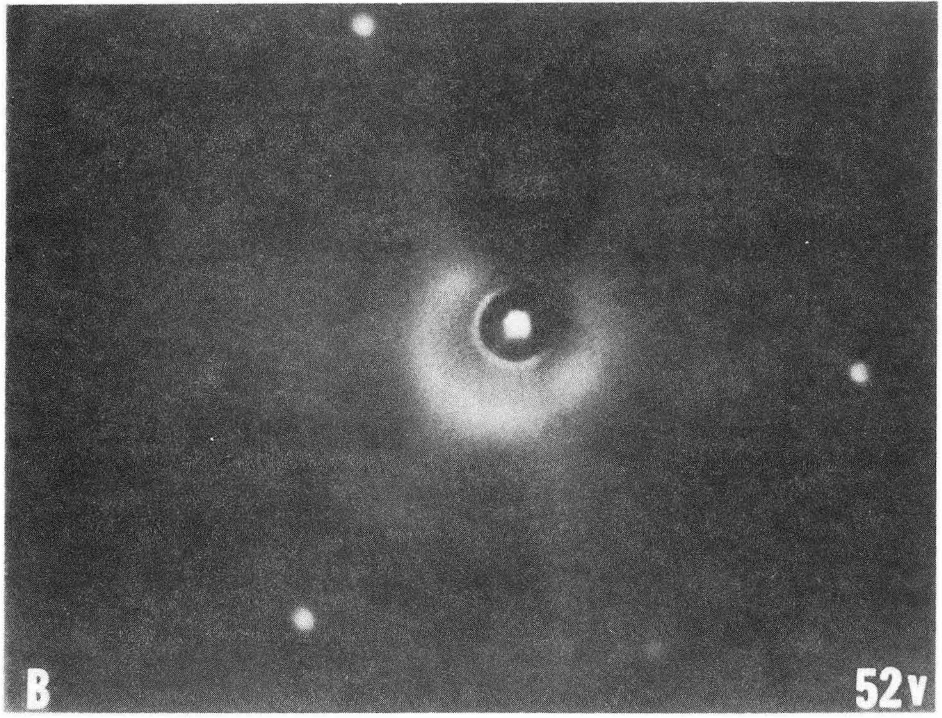
Mesitylene adsorbed on the Pt(100)-(5x1) surface causes the appearance of 1/3 order streaks, while the 1/5 order diffraction features characteristic of the (5x1) substrate structure remains. The diffraction pattern observed is shown in Figure 20. The WFC on adsorption is approximately -1.7V (Figure 21). Adsorption at higher pressures (~$4 \times 10^{-7}$ torr) causes the formation of a disordered adsorbed layer, the (5x1) diffraction features disappear and the WFC (-1.35V) is less than that during exposure at low pressures.

T-butylbenzene adsorption: The adsorption of tert-butylbenzene on the Pt(111) surface causes the formation of a largely disordered surface layer. Streaked high order features are visible for a short time after initial exposure but their intensity decreases rapidly with time. Finally, only diffraction features characteristic of a (1x1) surface structure with high background intensity are observed. The WFC on adsorption is approximately -1.7V; however, it depends on the initial incident flux (Figure 22).

Figure 18

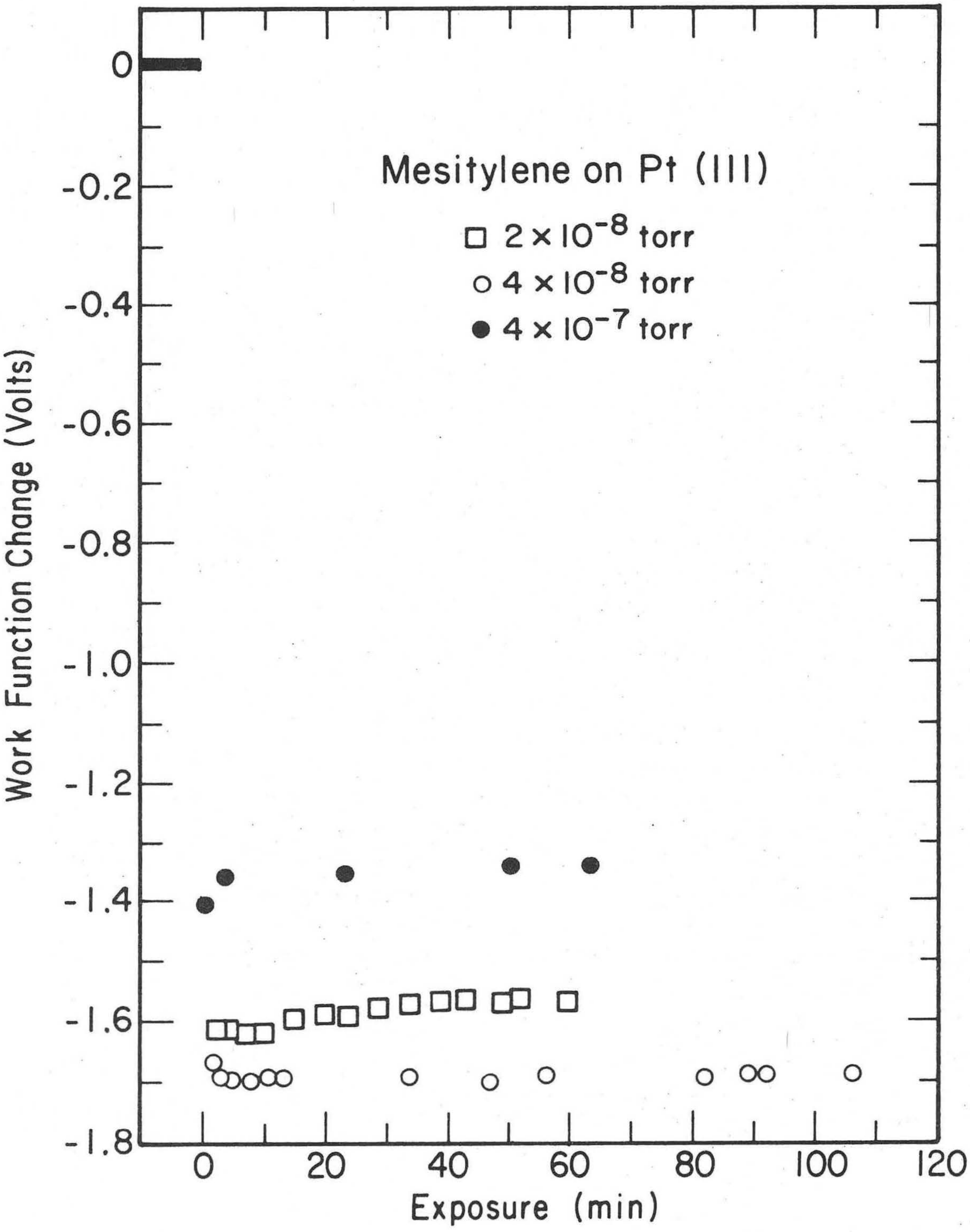


(a) The diffraction pattern resulting from mesitylene adsorption on the Pt(111) surface.



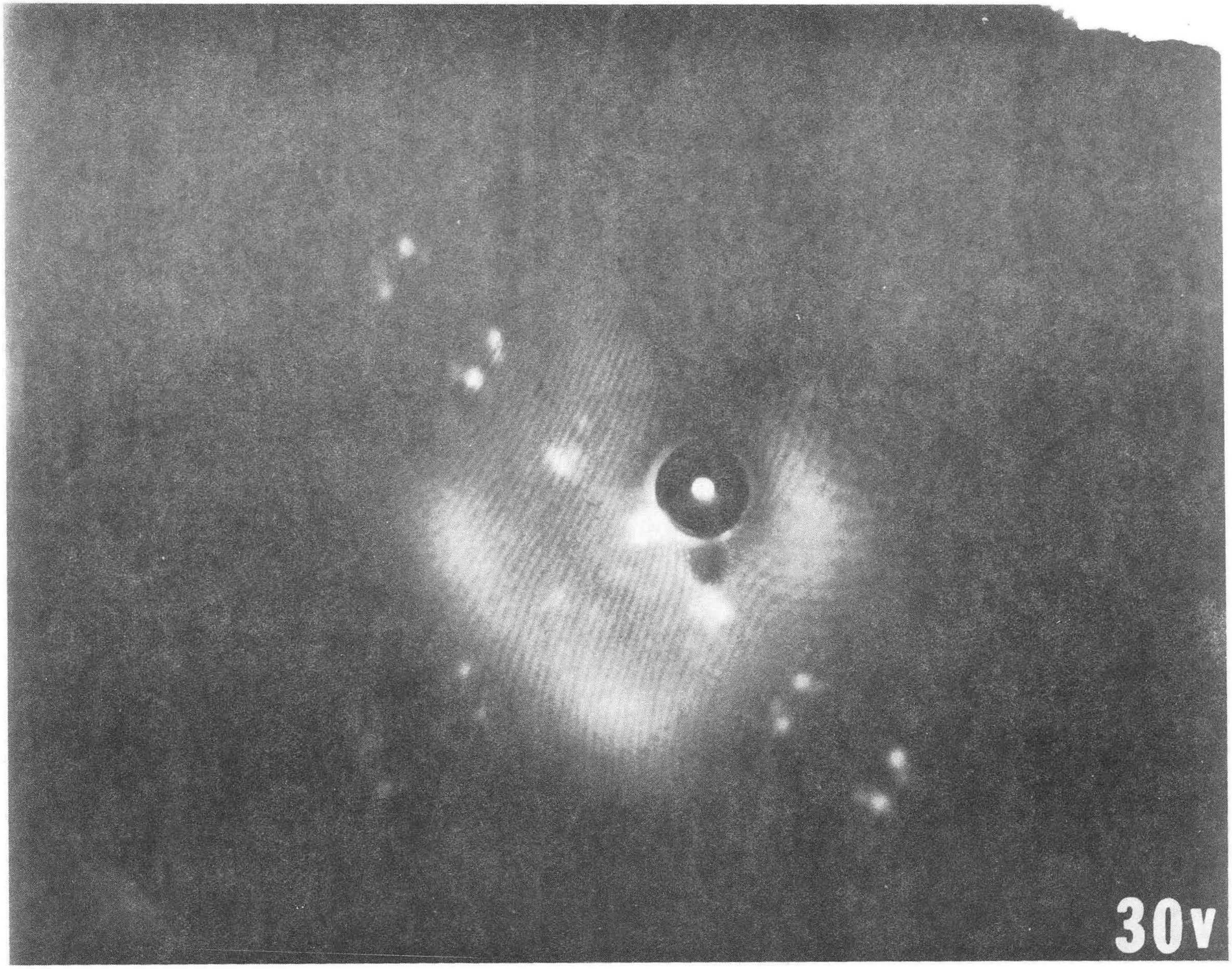
(b) The diffraction pattern resulting from mesitylene adsorption on the Pt(111) surface showing the first order Pt diffraction features.

XBB 732-685



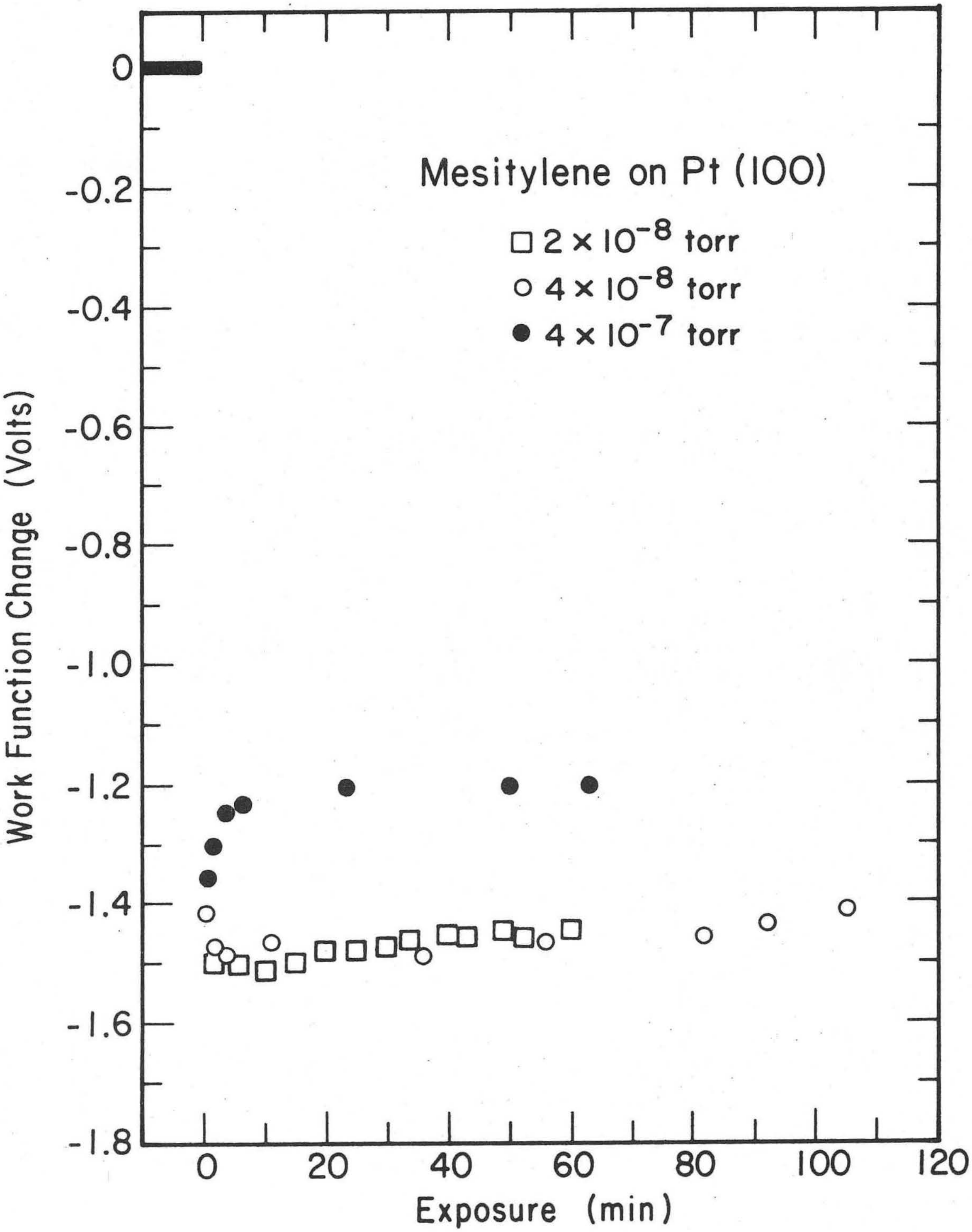
XBL 732-5758

Figure 19 Work function change as a function of time during mesitylene adsorption on the Pt(111) surface. The pressure should be multiplied by 6 to give the effective pressure at the surface.



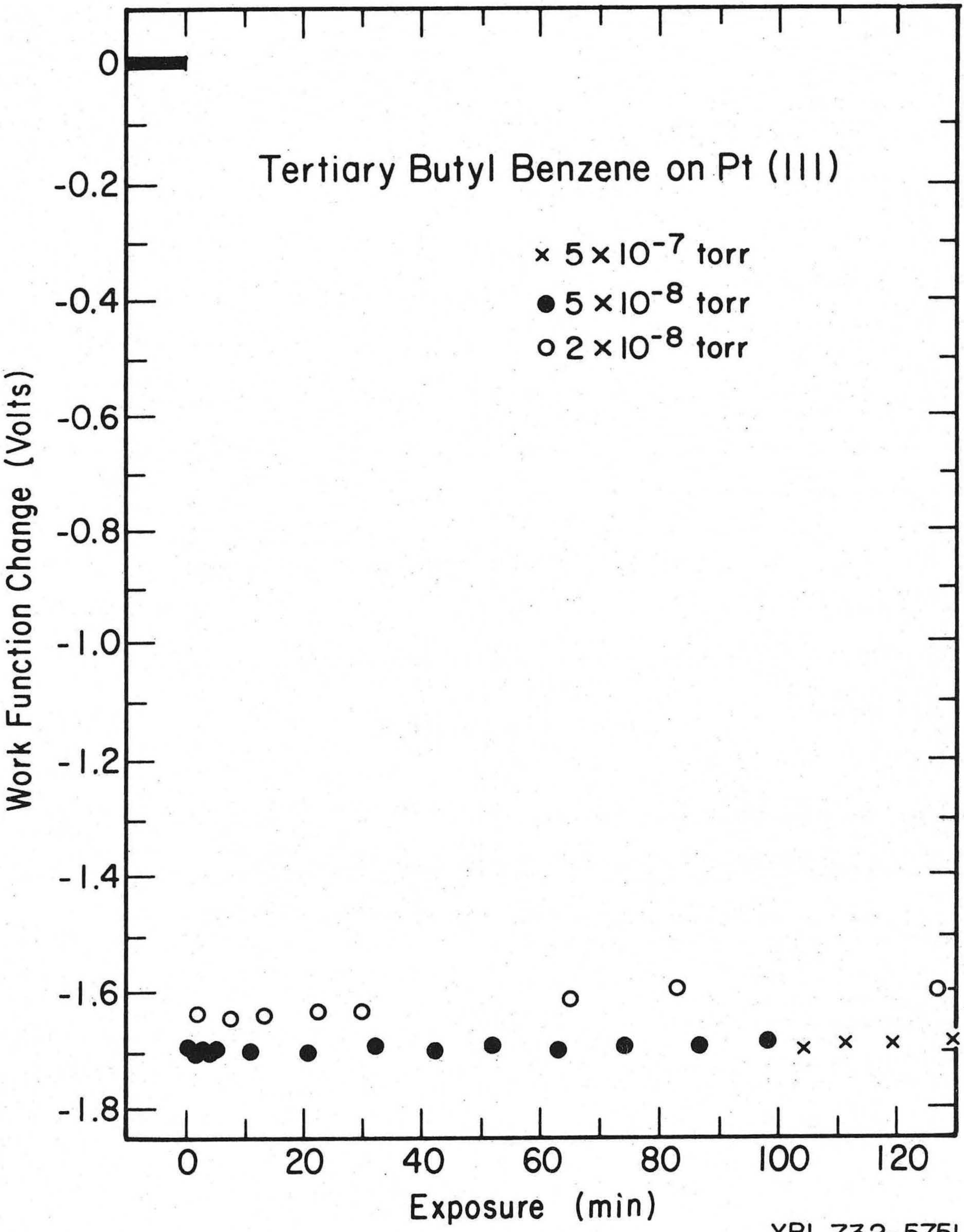
XBB 732-678

Figure 20 The diffraction pattern resulting from adsorption of mesitylene on the Pt(100)-(5x1) surface.



XBL 732-5759

Figure 21 Work function change as a function of time during mesitylene adsorption on the Pt(100)-(5x1) surface. The pressure should be multiplied by 6 to give the effective surface pressure.



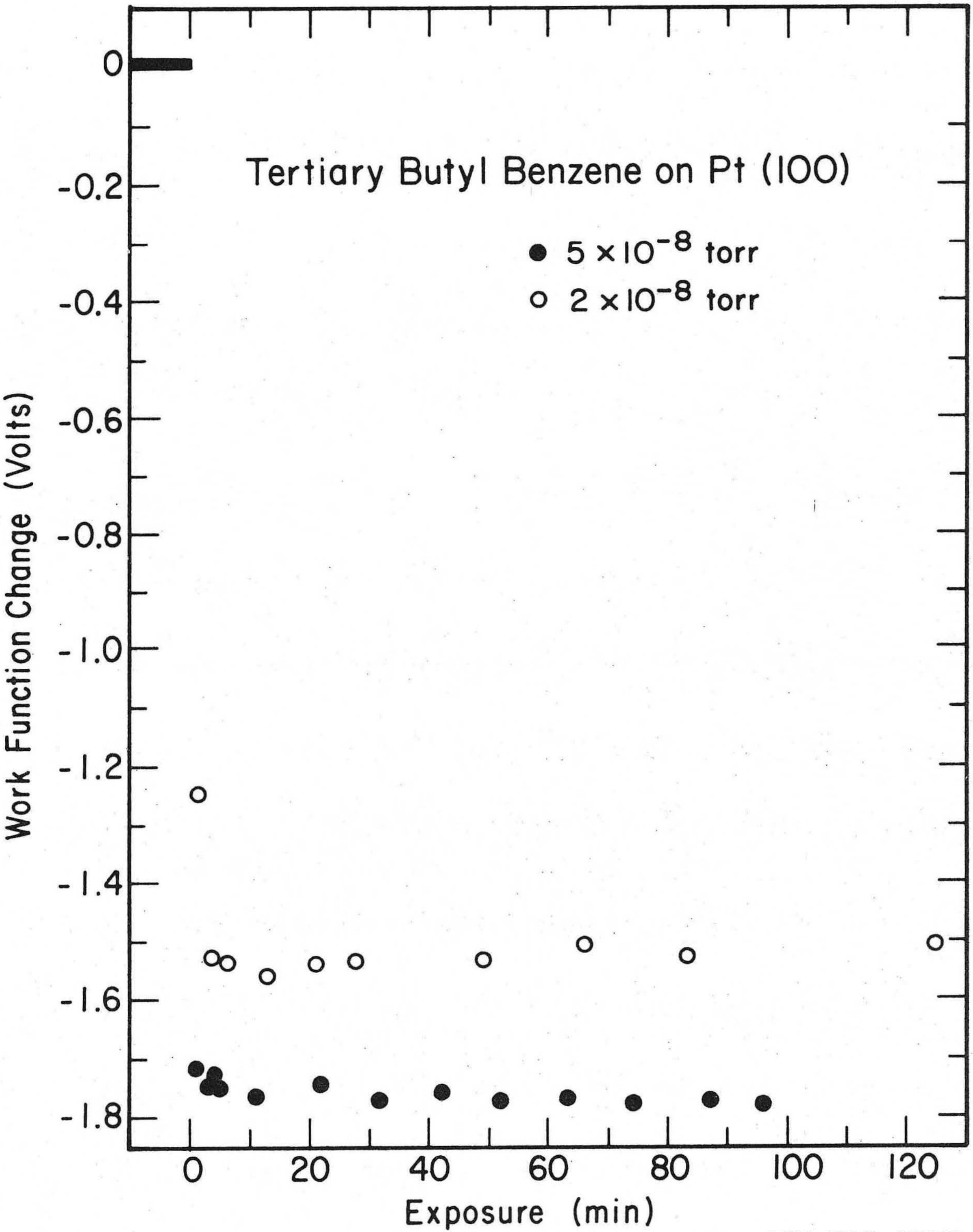
XBL 732-5751

Figure 22 Work function change on adsorption of t-butylbenzene on the Pt(111) surface. The pressure should be multiplied by 6 to give the effective pressure at the surface.

The adsorption of t-butylbenzene on the Pt(100)-(5xl) surface causes the disappearance of the diffraction features characteristic of the (5xl) substrate structure and an increase in the background intensity. The WFC on adsorption is approximately -1.75V (Figure 23); however, the WFC on adsorption depends on the initial incident vapor flux.

N-butylbenzene adsorption: N-butylbenzene adsorbed on the Pt(111) surface forms a very poorly ordered adsorbed layer. The degree of ordering is strongly dependent on the initial incident vapor flux. The faster the rate of deposition, the less ordered the adsorbed layer. A diffraction pattern taken after 6 minutes exposure at $8 \times 10^{-9}$ torr (recorded pressure) is shown in Figure 24b. The high intensity region terminates at 1/2 order with respect to the first order Pt diffraction features. The extra diffraction features disappear after approximately 20 minutes of exposure. That is, with continued exposure the initially poorly ordered structure becomes disordered. The WFC on adsorption is approximately -1.5V as shown in Figure 25. The WFC depends markedly on the initial incident vapor flux.

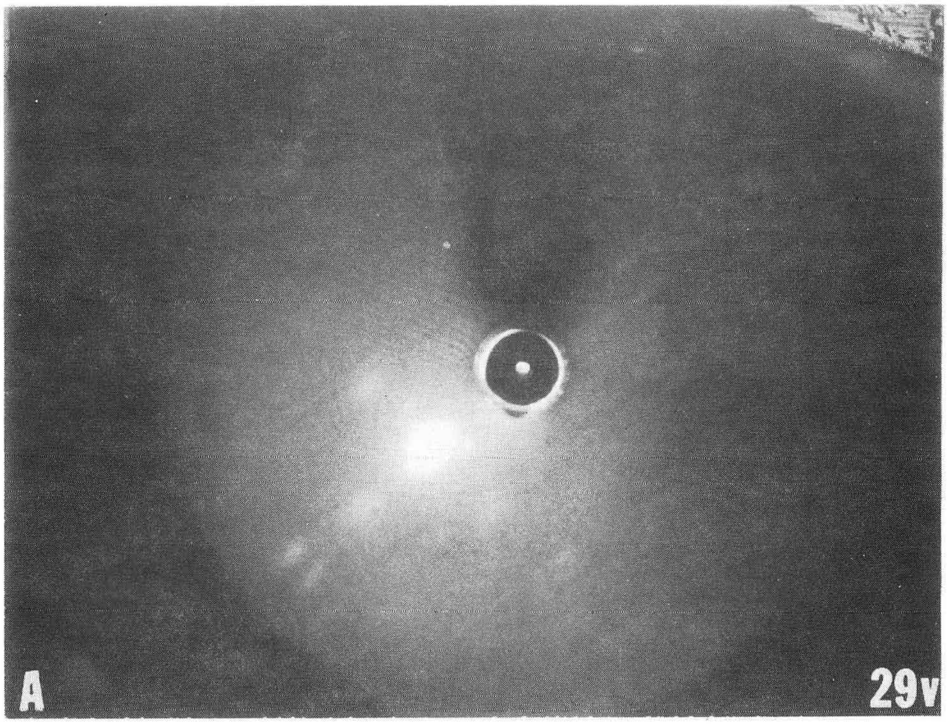
N-butylbenzene adsorbed on the Pt(100)-(5xl) surface causes the appearance of very faint high order streaks which disappear with continued exposure. The (5xl) diffraction features disappear at a slightly slower rate than the extra diffraction features due to the adsorbate. Figure 24a shows the diffraction pattern after 12 minutes exposure at $8 \times 10^{-9}$ torr recorded pressure. The WFC on adsorption, approximately -1.5V, is shown in Figure 26. It should be noted that the WFC is again strongly dependent on the initial incident vapor flux.



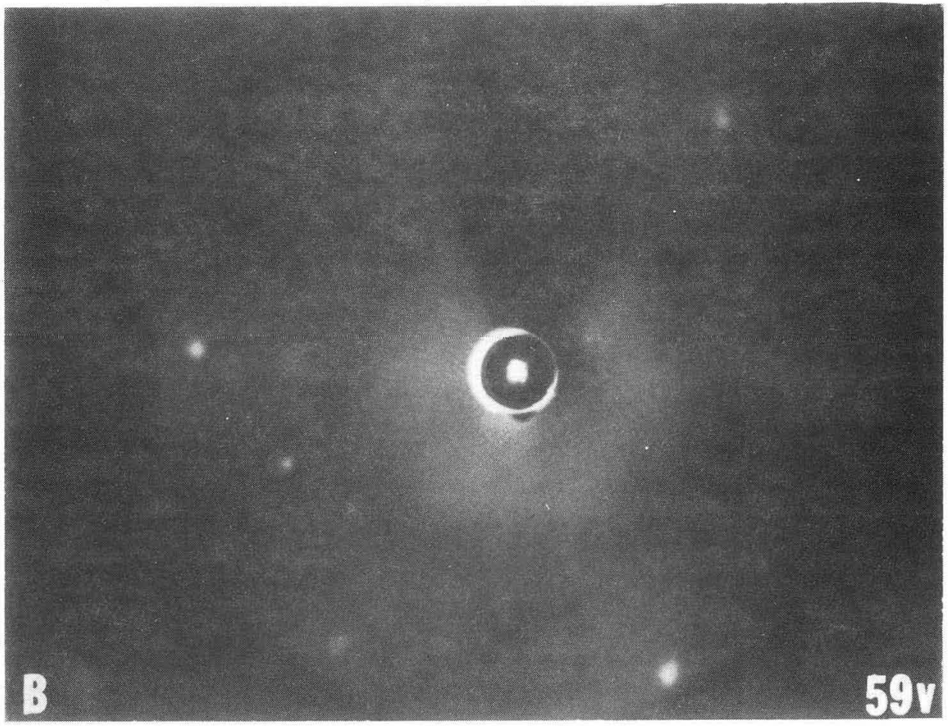
XBL732-5750

Figure 23 Work function change on adsorption of t-butylbenzene on the Pt(100)-(5x1) surface. The pressure should be multiplied by 6 to give the effective surface pressure.

Figure 24

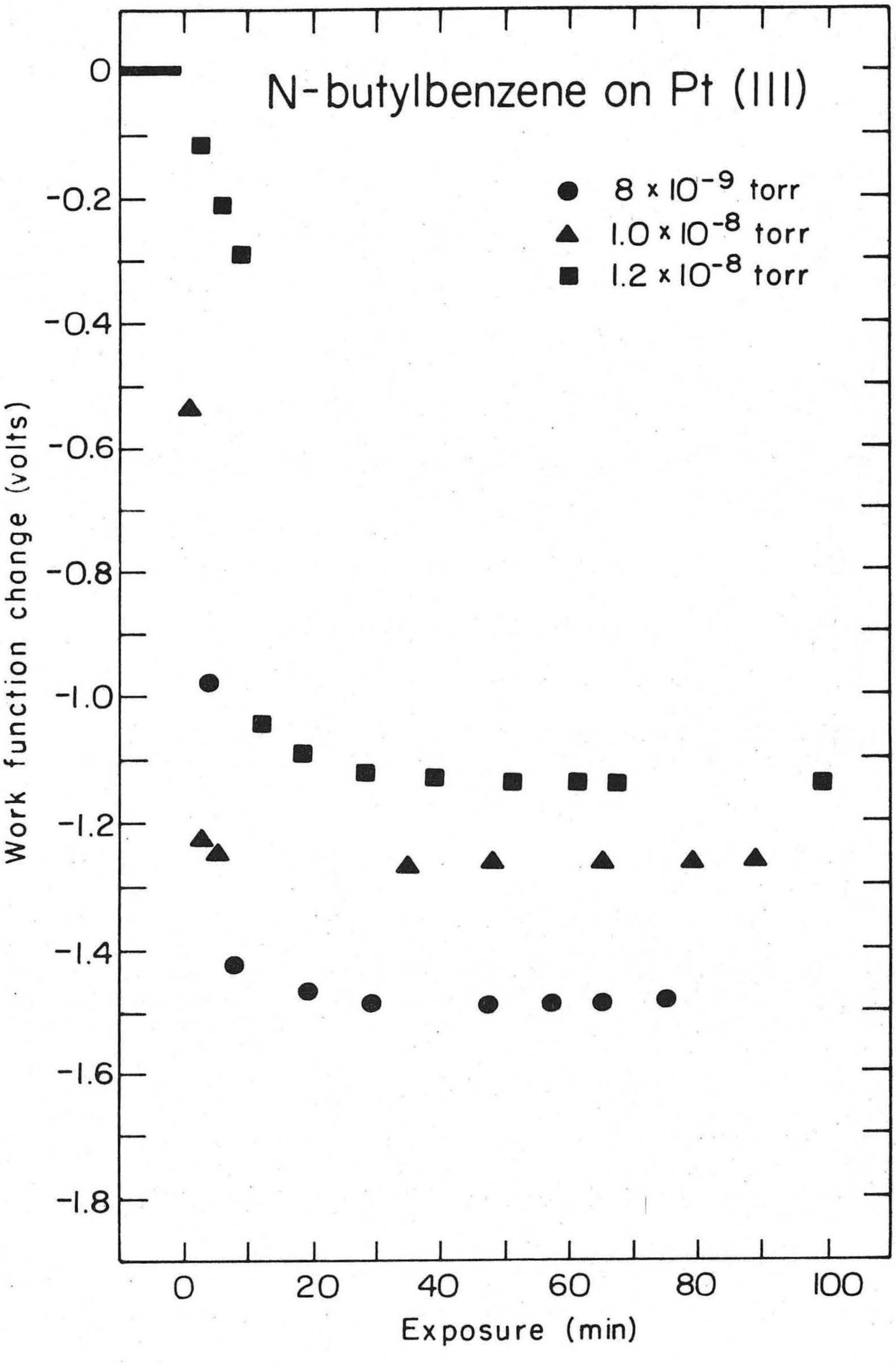


(a) The diffraction pattern resulting from adsorption of n-butylbenzene on the Pt(100)-(5x1) surface.



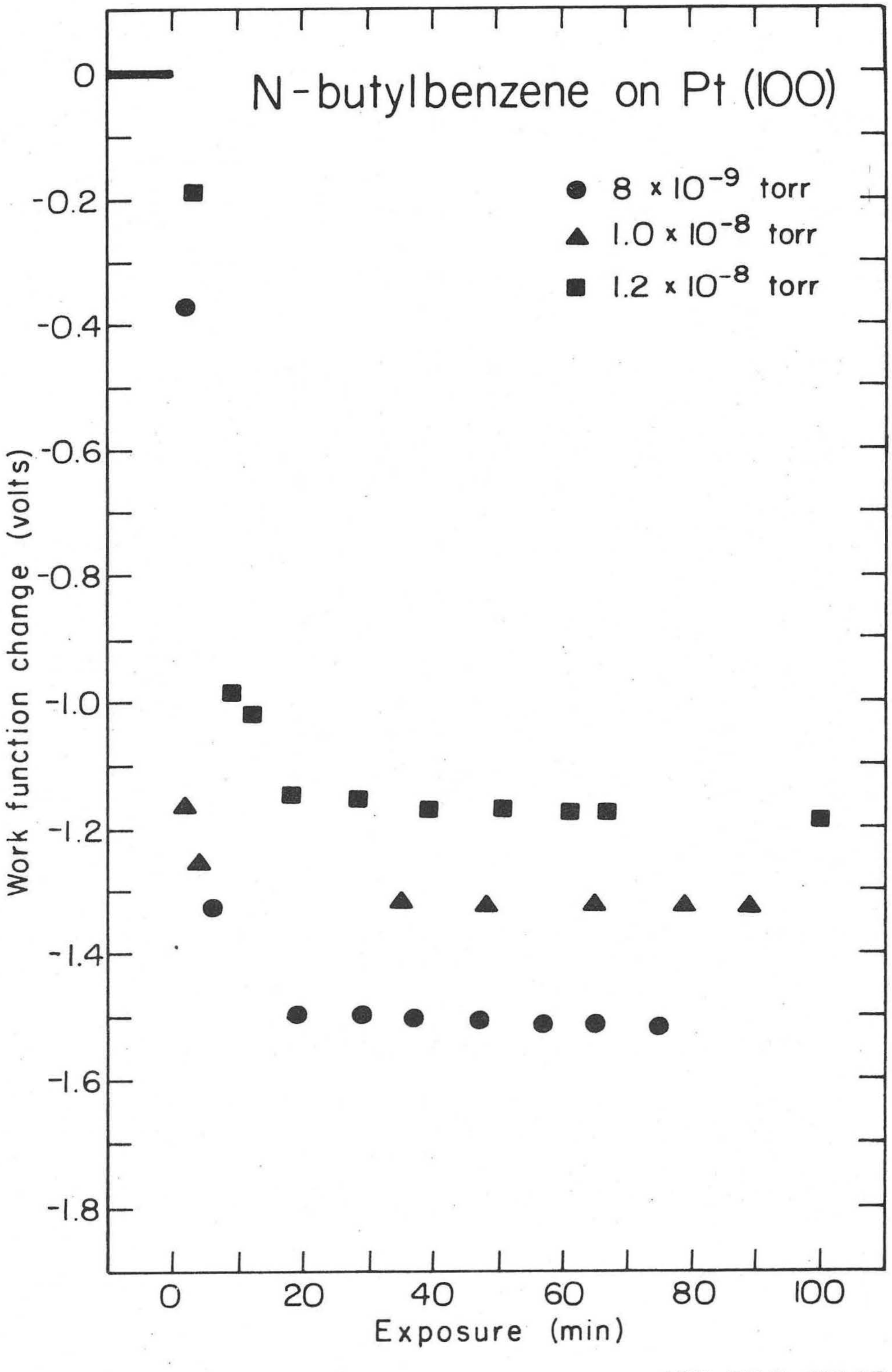
XBB 732-683

(b) The diffraction pattern resulting from adsorption of n-butylbenzene on the Pt(111) surface.



XBL732-5741

Figure 25 Work function change on adsorption of n-butylbenzene on the Pt(111) surface. The pressure should be multiplied by 6 to yield the effective surface pressure.



XBL 732-5740

Figure 26 Work function change on adsorption of n-butylbenzene on the Pt(100)-(5x1) surface. The pressure should be multiplied by 6 to yield the effective surface pressure.

Aniline adsorption: Aniline adsorbed on the Pt(111) surface causes the formation of a complex poorly ordered surface structure. The diffraction pattern (Figure 27) exhibits streaks at 1/3 order position along with diffraction spots at the 1/2 order position and several broad high intensity areas near 2/3 order position. The WFC on adsorption is approximately -1.8V as shown in Figure 28; however, the WFC depends on the initial incident vapor flux.

Aniline adsorption on the Pt(100)-(5x1) surface causes the diffraction features characteristic of the (5x1) structure to disappear and cause an increase in background intensity. However, there is no evidence for the formation of ordered structures from the diffraction pattern. The WFC on adsorption is approximately -1.75V as shown in Figure 29.

Nitrobenzene adsorption: Adsorption of nitrobenzene on the Pt(111) surface causes the formation of a fairly well-ordered layer with periodicity 3 times the underlying lattice as indicated by the diffraction pattern (Figure 30). The WFC on adsorption is approximately -1.5V as shown in Figure 31. However, the degree of ordering and the WFC depend on the total amount of electron bombardment which has occurred. The initially ordered layer becomes disordered during approximately 7 minutes of exposure to a 30V electron beam at 2 x $10^{-6}$ amps.

Nitrobenzene adsorbed on the Pt(100)-(5x1) surface causes the (5x1) diffraction features to disappear and very faint diffuse high order features to appear. These weak high order features are too faint to photograph. The WFC on adsorption is approximately -1.4V as shown in Figure 32.

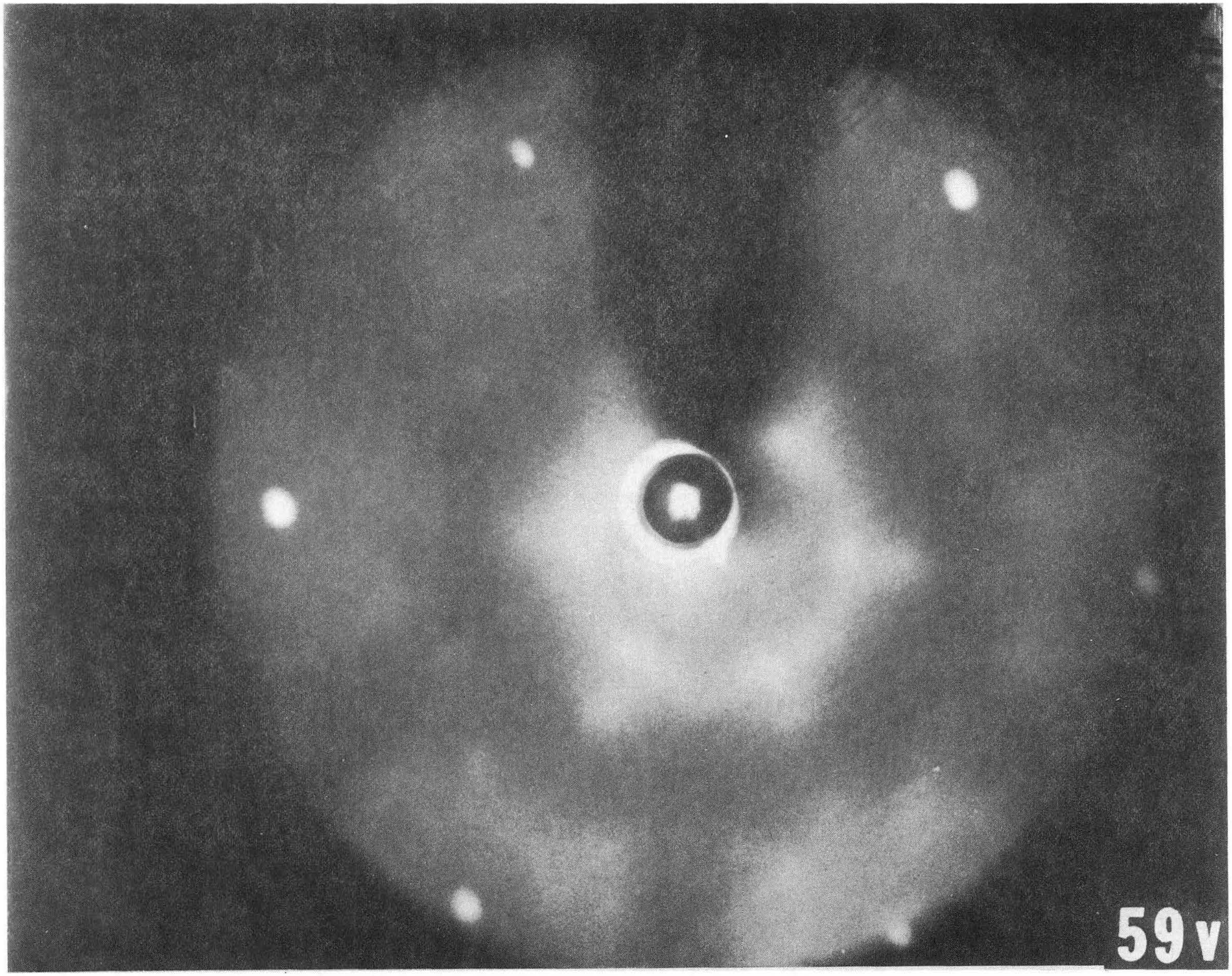
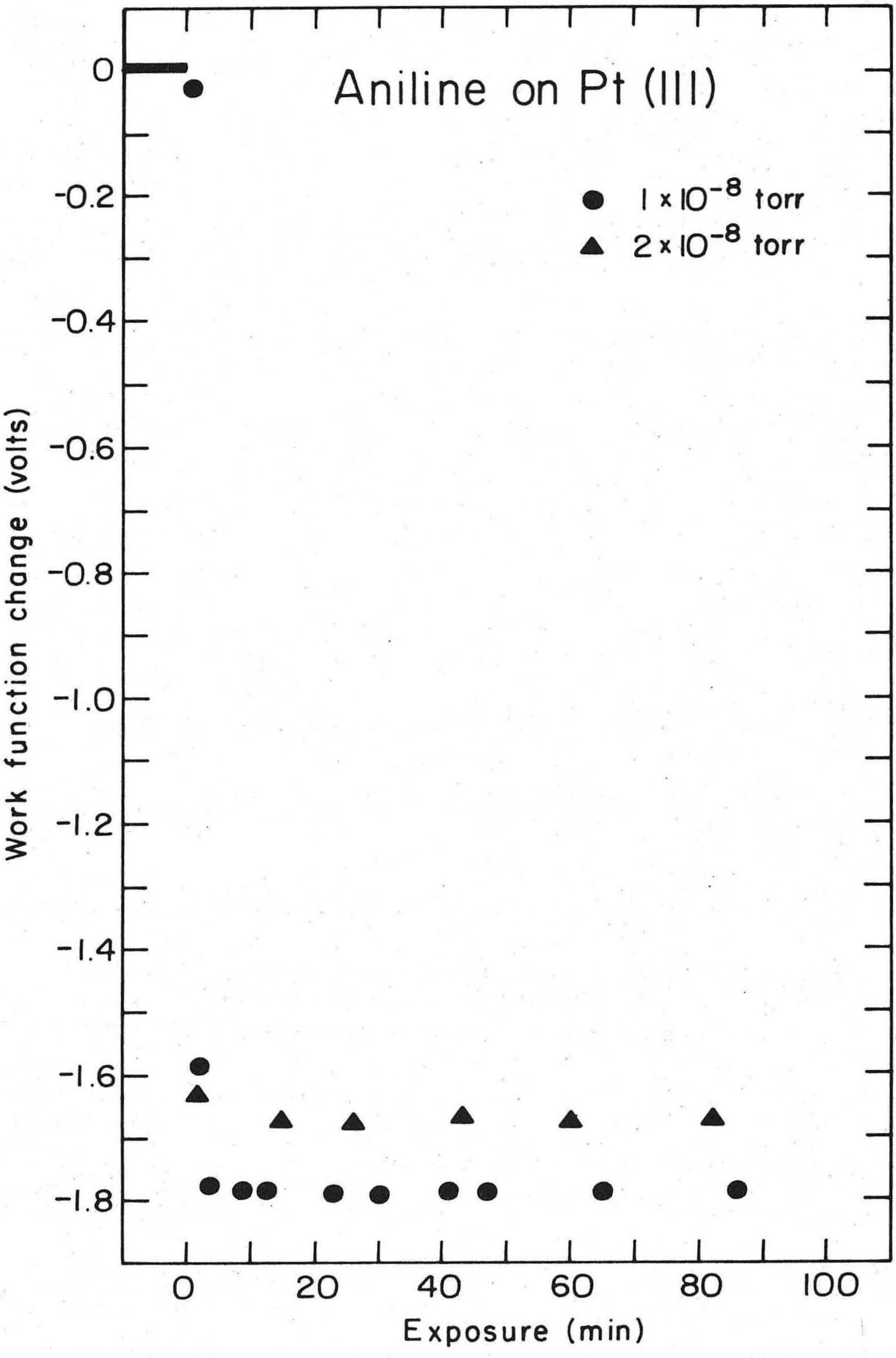


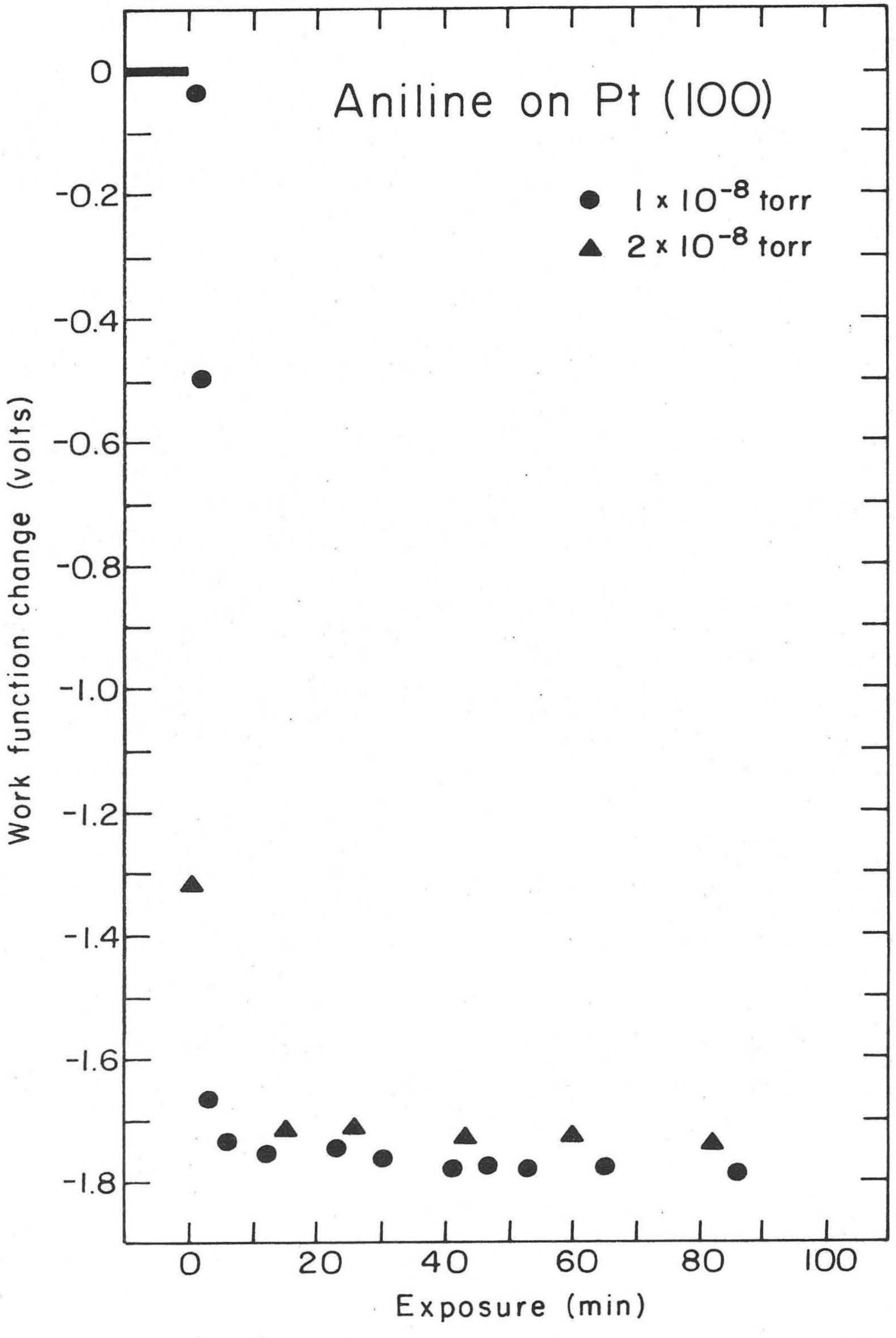
Figure 27 The diffraction pattern resulting from aniline adsorption on the Pt(111) surface. The first order Pt diffraction features are also visible.

XBB 732-677



XBL 732-5743

Figure 28 Work function change on adsorption of aniline absorbed on the Pt(111) surface. The pressure should be multiplied by 6 to yield the effective pressure at the surface.



XBL 732-5742

Figure 29 Work function change on adsorption of aniline on the Pt(100)-(5x1) surface. The pressure should be multiplied by 6 to yield the effective surface pressure.

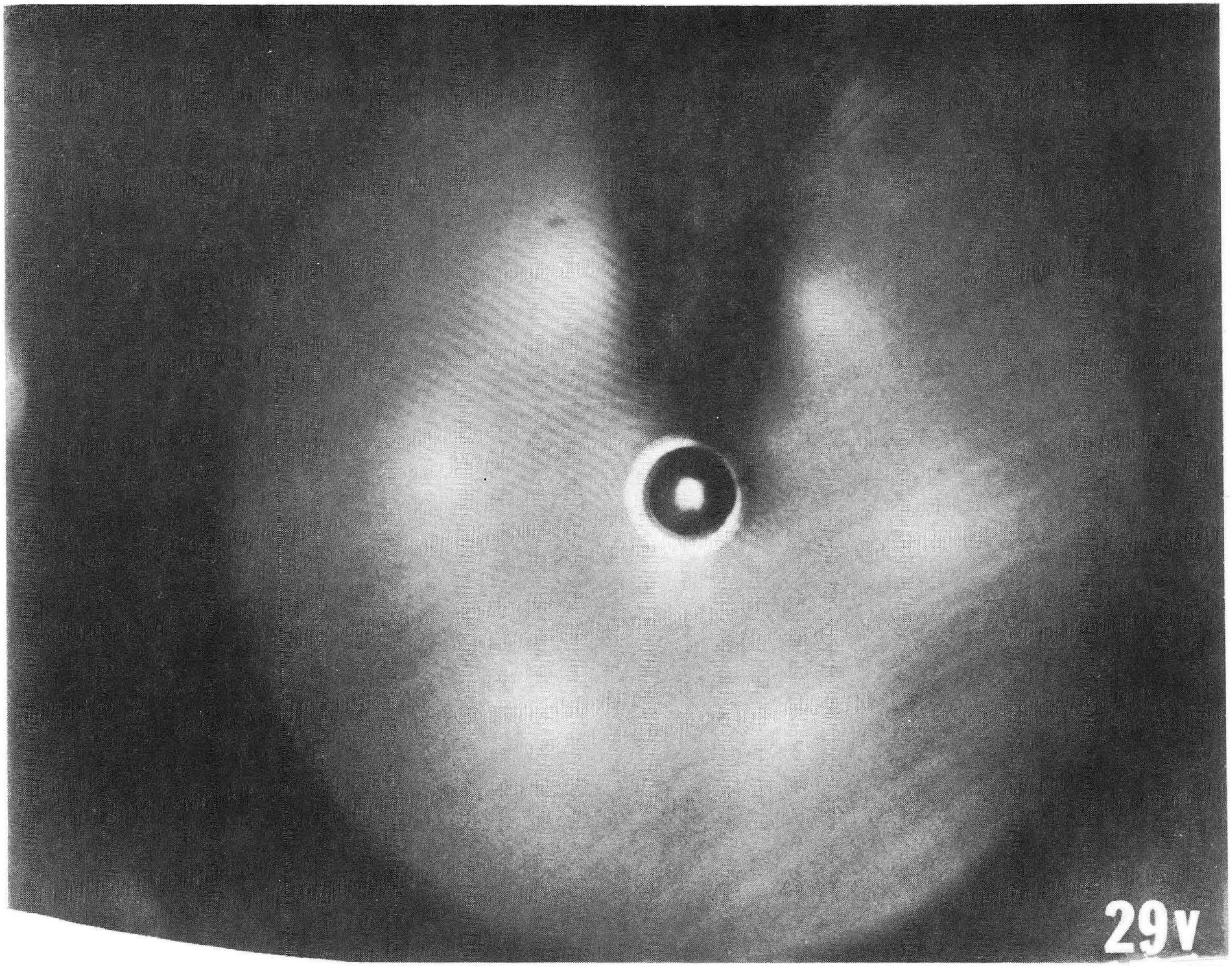


Figure 30 The diffraction pattern resulting from nitrobenzene adsorption on the Pt(111) surface.

XBB 732-674

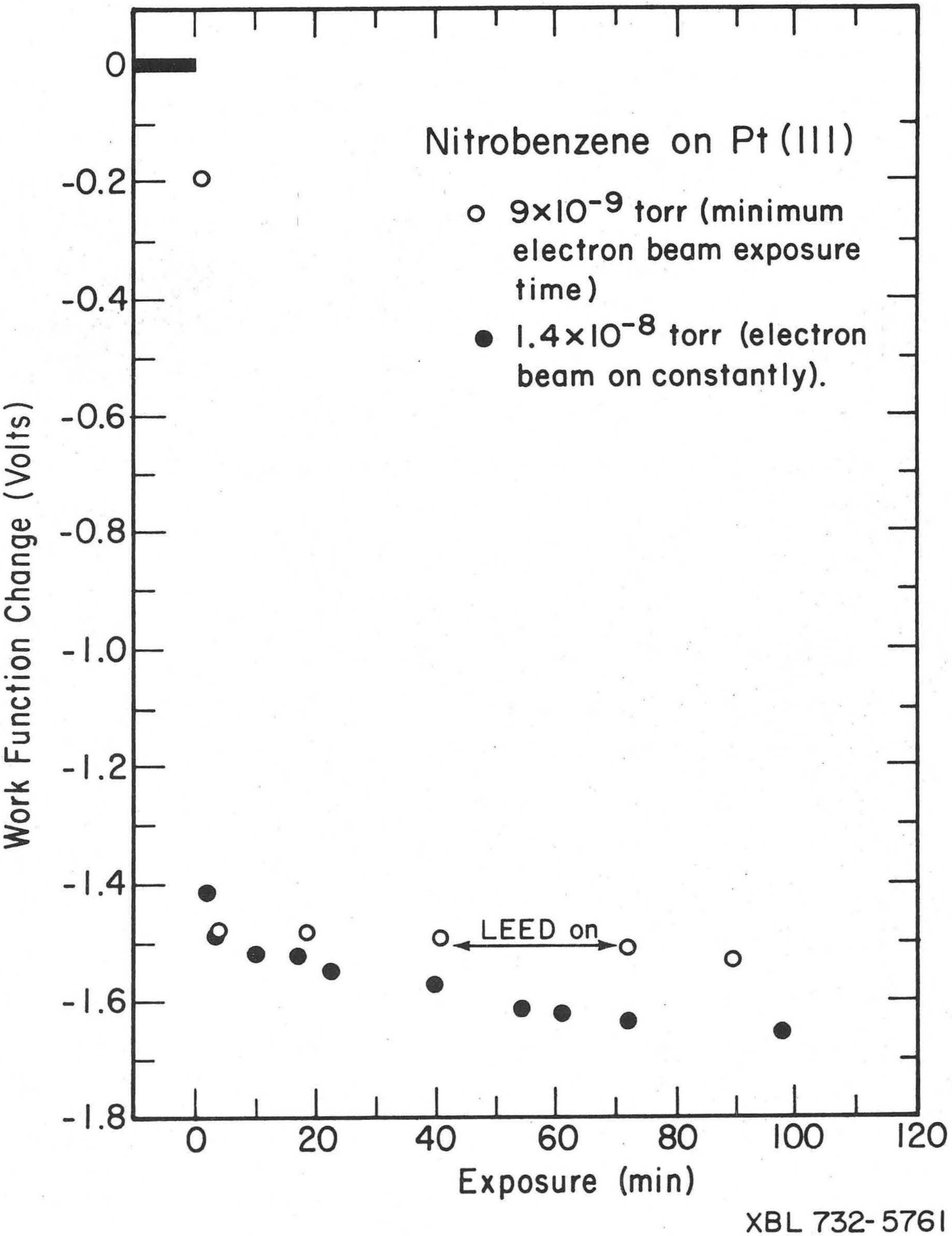


Figure 31 Work function change on adsorption of nitrobenzene on the Pt(111) surface. The pressure should be multiplied by approximately 6 to yield the effective surface pressure.

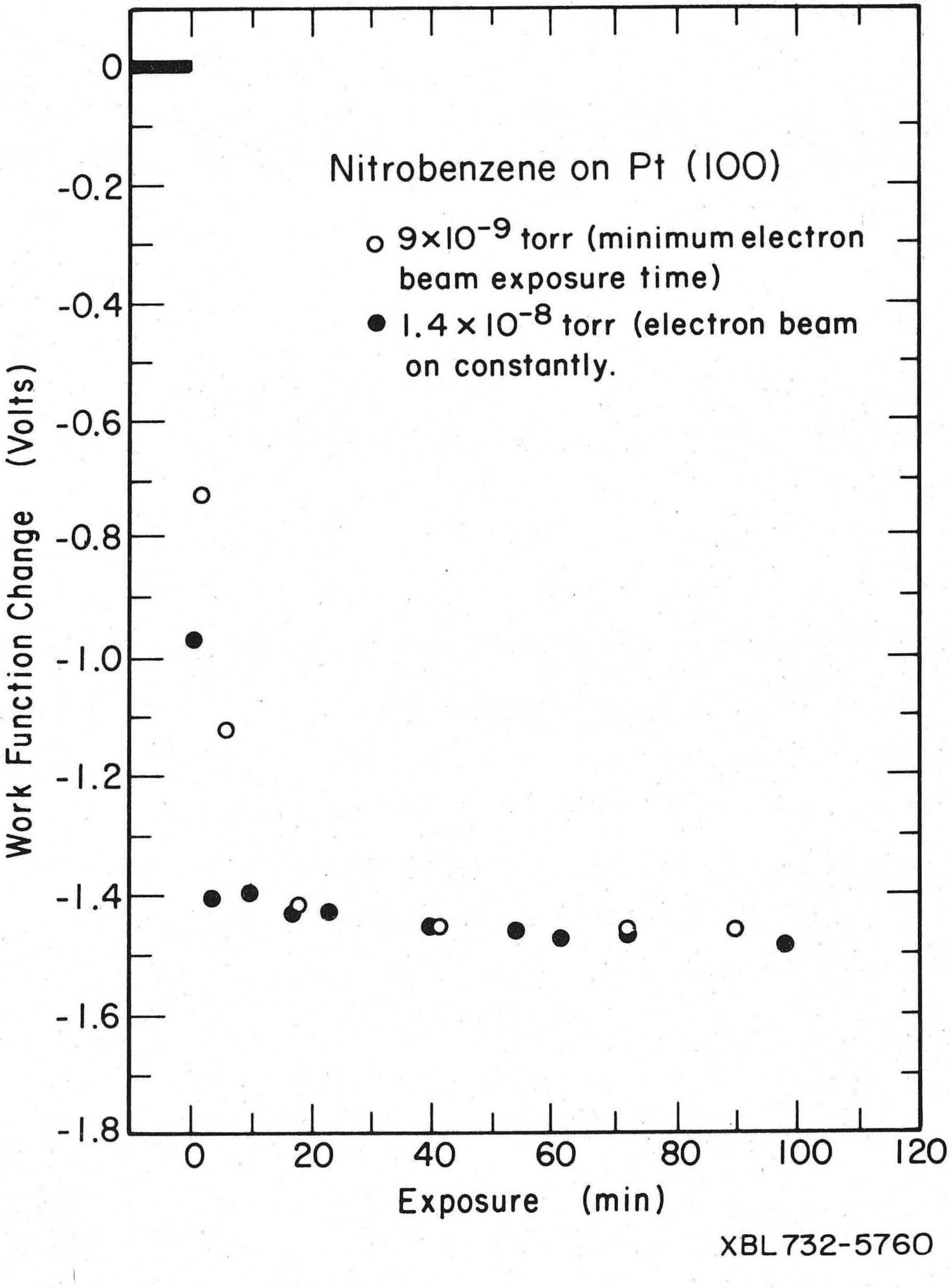


Figure 32 Work function change resulting from nitrobenzene adsorption on the Pt(100)-(5x1) surface. The pressure should be multiplied by 6 to yield the effective surface pressure.

Cyanobenzene adsorption: Adsorption of cyanobenzene on the Pt(111) surface causes the appearance of diffuse 1/3 order diffraction features (Figure 33). The extra diffraction feature slowly became less prominant during continued exposure. The work function change on adsorption is approximately -1.6V as shown in Figure 34.

Adsorption of cyanobenzene on the Pt(100)-(5x1) surface causes an increase in the background intensity and a slow decrease in the intensity of the (5x1) diffraction features which were still visible after 60 minutes of exposure. The work function change on adsorption is approximately -1.5V as shown in Figure 35.

Temperature effects: In general, an increase in substrate temperature to 150°C with continued exposure causes disordering of the ordered adsorbate surface structures. The WFC which accompanies these changes in order indicates little variation. Thus, there seems to be no significant change in either the density or composition of the adsorbed layer. Increasing the substrate temperature to 250-300°C during continued exposure to the vapor molecules results in a decrease in the magnitude of the WFC indicating decomposition of the adsorbed layer. The WFC measurements were made by heating the samples in organic vapor flux and then cooling for 15 minutes in vapor flux before taking the WFC. This procedure minimized the possibility of change of surface coverage due to desorption at elevated temperatures. Heating to 900-950°C during continued exposure to the vapor flux causes the appearance of a graphitic overlayer[6-10] with a WFC of approximately -1.1V with respect to the clean metal surface. This value is in

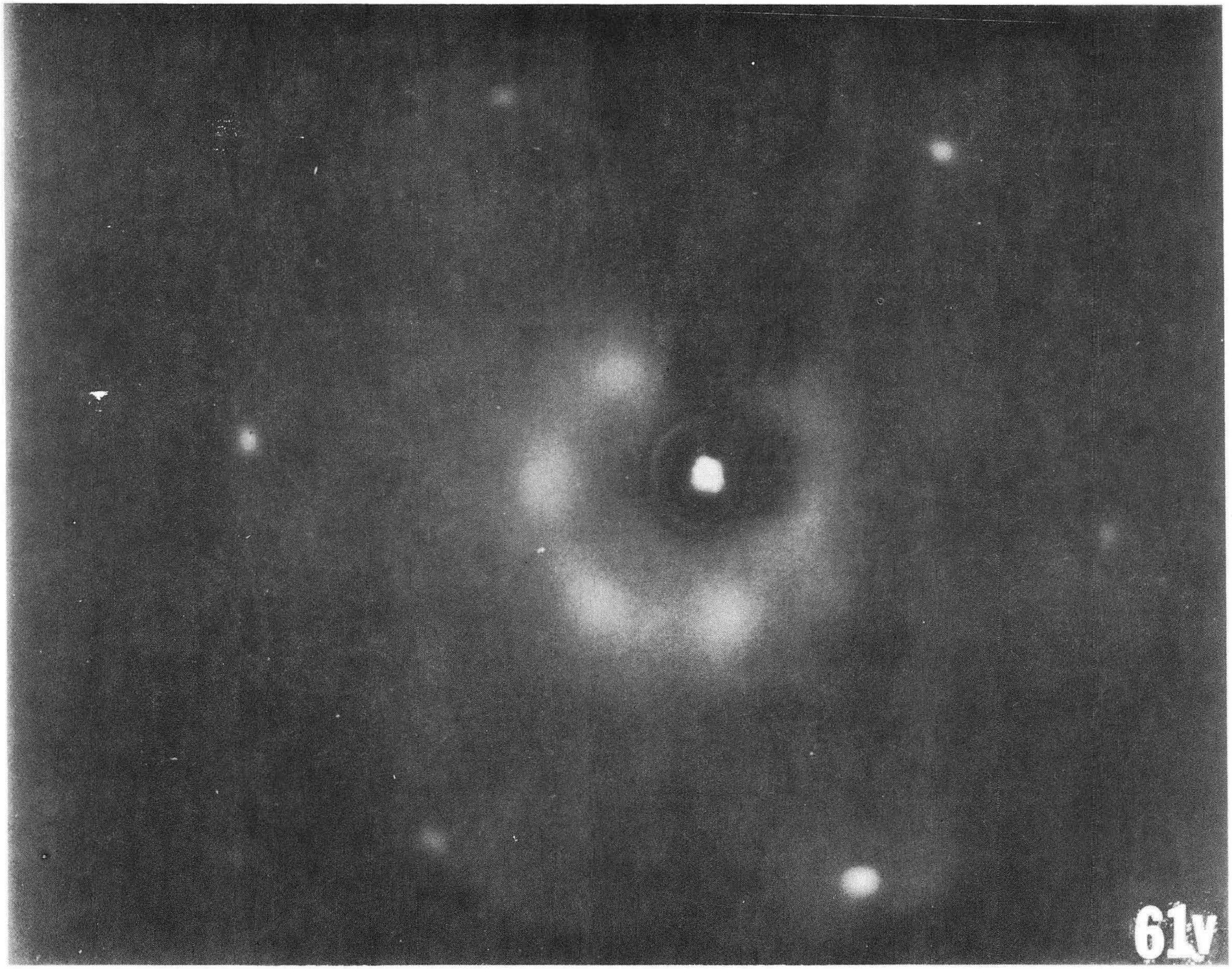
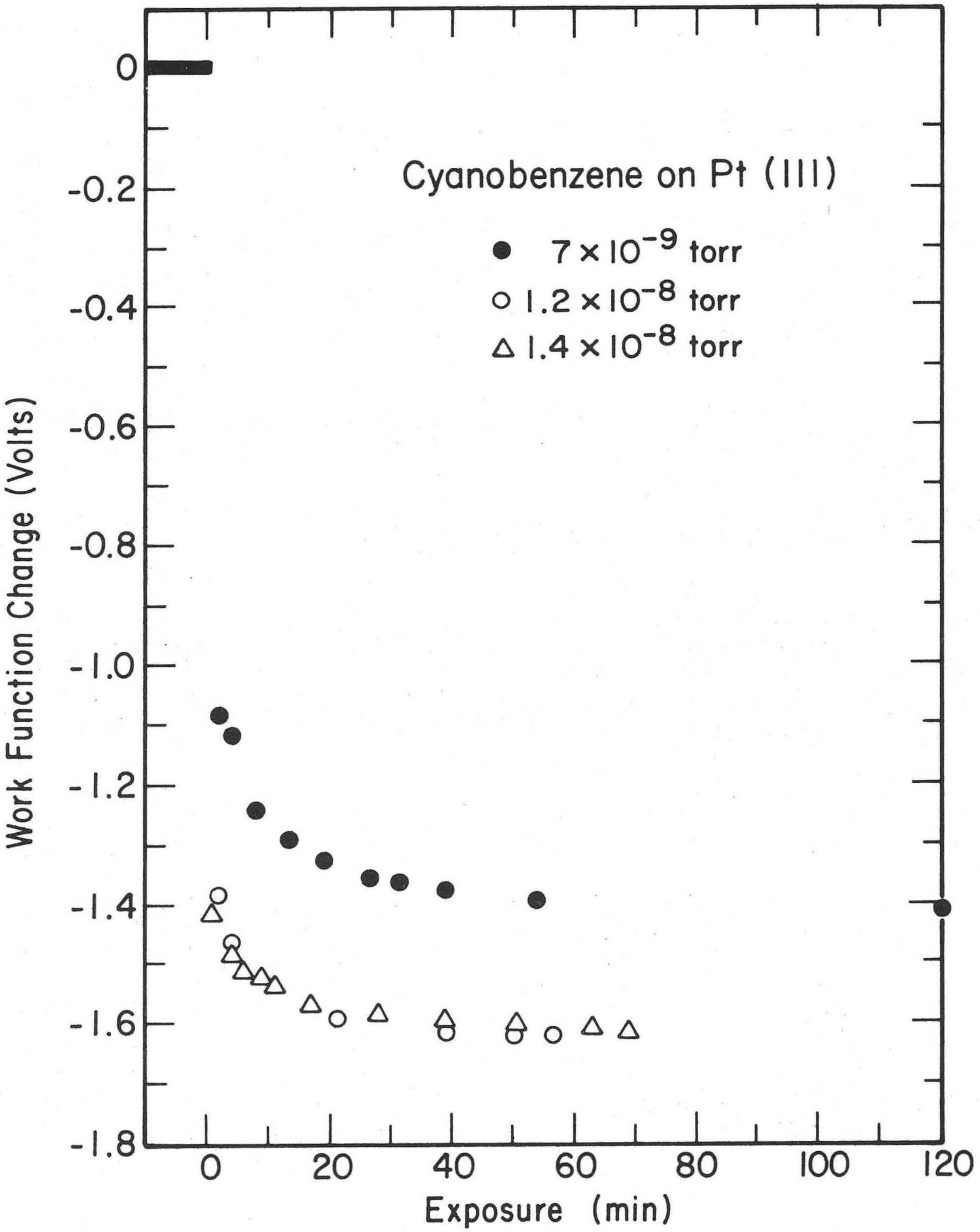
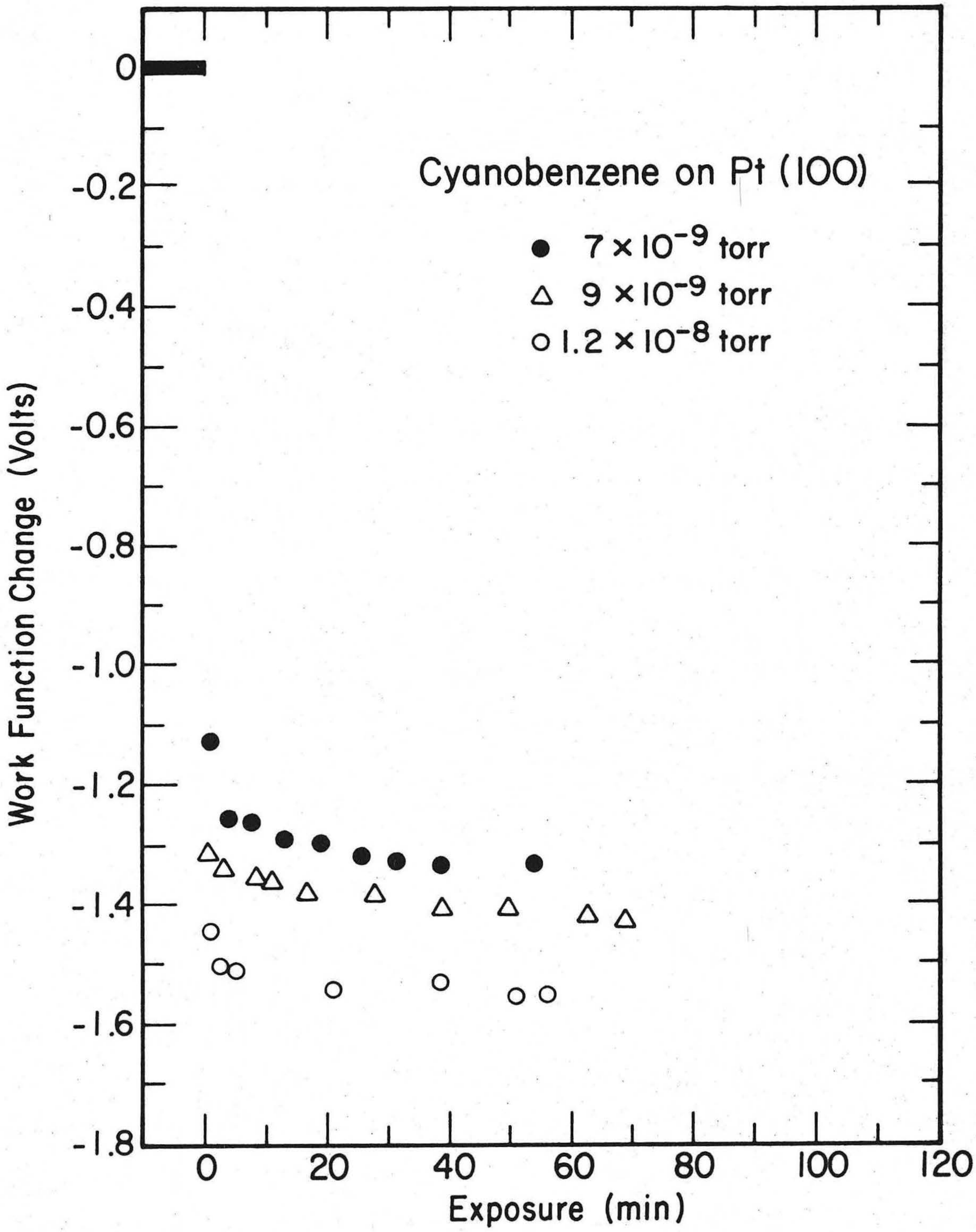


Figure 33 The diffraction pattern resulting from cyanobenzene adsorption on the Pt(111) surface. The first order Pt diffraction features are also visible.



XBL732-5753

Figure 34 Work function change on adsorption of cyanobenzene on the Pt(111) surface. The pressure should be multiplied by 6 to yield the effective surface pressure.



XBL732-5752

Figure 35 Work function change on adsorption of cyanobenzene on the Pt(100)-(5x1) surface. The pressure should be multiplied by approximately 6 to yield the effective surface pressure.

agreement with the $\Delta\phi$ expected because of the difference in work functions for polycrystalline platinum (measured by several techniques[11-13]) ($\phi \simeq$ 5.6-5.8V) and for polycrystalline graphite[7] ($\phi \simeq 4.4$V).

In those cases for which the (5x1) surface structure is present on the Pt(100) substrate after adsorption, heating to 150°C causes the (5x1) structure to disappear. There is no WFC accompanying the disappearance of the (5x1) pattern which indicates negligible change in charge transfer between adsorbate and the platinum substrate with the relaxation of the reconstructed surface.

## Discussion

All organic molecules reported in this paper adsorb on both the (111) and (100) crystal surfaces of platinum. Ordering in the adsorbed layer was more pronounced on the Pt(111) surface than on the Pt(100)-(5x1) surface. The aromatic molecules which have small substituent groups or high rotational symmetry form more ordered overlayers under the experimental conditions employed. Thus, the shape of the adsorbate molecules and the rotational symmetry of the substrate determines the degree of ordering which occurs in the adsorbed layer.

We have also found that the WFC on adsorption and the degree of ordering in the overlayer varies with the initial rate of growth of the adsorbed layer which can be varied by changing the incident vapor flux. In general, for the hydrocarbons studied, the slower the rate of growth (smaller the incident flux), the larger the WFC change and the more ordered the overlayer. These observations seem to indicate that with low incident vapor flux the density of the adsorbed layer may be increased because of more efficient packing in the ordered overlayer. With slow growth rates, the size of the ordered domains is being increased in the adsorbed layer, leading to an increase in the density of surface sites occupied by the adsorbate.

Both of these observations (1. High symmetry promotes ordered surface structure formation. 2. Slow growth of the adsorbed layer promotes ordered structure formation.) can be explained by a simple model of ordering for adsorbed aromatic systems on Pt surfaces. Ordered adsorption for these large molecules may proceed by a two-step mechanism. Initially the aromatic molecules may adsorb on the surface in a disordered fashion. The second step involves ordering of the adsorbed layer and indicates the importance of surface diffusion (either translational or rotational) in this ordering process. If the adsorbate has a shape which approximates a circular cross section, reorientation into ordered layers is less difficult than reorientation of adsorbates with bulky side groups. Slow deposition of the overlayer allows adsorbed molecules more reorientation time before becoming locked into place by a large number of neighbors. This type of ordering should be distinguished from ordering caused by site adsorption. Site adsorption involves adsorption into a specific surface site in a specific orientation. Ordering results because the surface sites are ordered. During site adsorption, adsorption and ordering occur simultaneously.

The WFC observed on adsorption ranges from -1.4V for nitrobenzene to -1.8V for aniline. Charge transfer of such magnitude indicates extensive interactions of the aromatic π systems with the substrate. Recent studies with other simple π bonded systems[2] indicate similar values of WFC on adsorption (ethylene on Pt(111), $\Delta\phi = -1.5V$; ethylene on Pt(100)-(5x1), $\Delta\phi = -1.25V$; acetylene on Pt(111) and Pt(100)-(5x1), $\Delta\phi = -1.65V$). Earlier studies of the adsorption of naphthalene[1] on the Pt(111) and Pt(100)-(5x1) surfaces indicate that $\Delta\phi = -2.0V$ for naphthalene adsorbed on Pt(111) and $\Delta\phi = -1.75V$ on the Pt(100)-(5x1) surface. For this case, π bonding seems to be substantiated by the unit cell size observed.

The interpretation of the diffraction information in these studies has been complicated by the absence of well-defined diffraction features. The diffraction features may be characteristic of the size and orientation of the unit cell in the ordered adsorbed layer or they may be characteristic of a coincidence distance between the adsorbed lattice and the substrate lattice. Previous studies involving ordered adsorption of organic molecules on single crystal platinum surfaces have indicated that either situation may occur.[1,2] Specifically, benzene forms coincidence lattices on the Pt(111) surface while naphthalene forms a structure for which molecular size is easily related to the unit mesh determined from the diffraction pattern. With these facts in mind, we have used the available chemical information, molecular dimensions, the observed WFC and the diffraction information to analyze the nature of the interaction between adsorbate and substrate.

Several preliminary experiments indicate that adsorption at higher pressure may induce dramatic changes in the interaction between substrate and adsorbate.[1] The results quoted in this paper should be used with caution in interpretation of higher pressure results.

## I. Toluene, M-xylene, Mesitylene, T-butylbenzene, and N-butylbenzene Adsorption on the Pt(111) Surface

### A. Work Function Change

The maximum WFC observed on adsorption for these compounds is listed in Table I. The values range from -1.5V for n-butylbenzene to -1.8V for m-xylene. This large electron transfer from the adsorbed molecules to the metal substrate implies that the polarizable $\pi$ electrons are involved extensively in the interaction between adsorbate and substrate. The similarity of the WFC on adsorption for this family of compounds also indicates that the primary interaction occurs between the aromatic $\pi$ system and the substrate surface since the benzene ring is the only structural entity common to all molecules in the series. If the aromatic $\pi$ system is the primary interaction center, it follows that the adsorption geometry should be similar for this family of compounds. In the absence of dehydrogenation the aromatic systems would be expected to adsorb parallel or nearly parallel to the substrate surface so that the aromatic $\pi$ system could efficiently interact with the substrate surface.

That these aromatic systems are adsorbed parallel or nearly parallel to the surface is further supported by the results of the mesitylene adsorption studies carried out at low pressure ($10^{-9}$ torr). Each aromatic hydrogen in mesitylene has adjacent methyl groups. Since methyl groups are known to deactivate the exchange of adjacent hydrogens in hydrogen-deuterium exchange studies, there should be little chance for dehydrogenation of the aromatic hydrogens and for subsequent interaction of the dehydrogenated site with the surface to form $\sigma$ (electron pair) bonds. Excluding demethylation, the only alternative for interaction appears to be $\pi$ bonding with the substrate surface. That is, mesitylene should be fairly inactive toward any type of interaction except $\pi$ bonding. The fact that its WFC on adsorption is similar to the WFC of other aromatic adsorbates supports our contention that the primary interaction occurs via $\pi$ bonding.

N-butylbenzene induces the smallest WFC on adsorption; the WFC on adsorption also depends markedly on the growth rate of the adsorbed layer. Both of these effects are caused by the presence of the long side chain which makes efficient packing in the surface plane difficult.

### B. Diffraction Studies

The diffraction patterns observed for this family of compounds indicate poor ordering of the adsorbed layer. For the series toluene, m-xylene, mesitylene adsorbed at room temperature, streaked diffraction features appear at 1/3, 1/2.6, 1/3.4 of the distance between the (00) beam and the first order platinum features. The unit cell size implied by these streaked features does not correlate with the molecular size of the adsorbed species since they are listed in order of increasing size above (the distance to the first order diffraction should vary inversely with the size of the adsorbed molecules). However, the diffraction patterns become better ordered in the series toluene, m-xylene, mesitylene. T-butylbenzene and n-butylbenzene on the other hand form disordered adsorbed layers.

Thus, it appears that large π-bonded adsorbed molecules of the same rotational multiplicity order more easily in the absence of long side-chains.

Detailed information concerning molecular orientation cannot be extracted from the diffraction patterns since poorly ordered layers are formed. However, it seems worthwhile to point out that toluene adsorbed parallel to the surface fits into the (3x3) unit cell observed while m-xylene and mesitylene do not fit into the (2.6x2.6) and (3.4x3.4) unit cells, respectively, which can be deduced from the diffraction features. The Pt(111)-(4x2)-toluene structure which forms at 150°C does not have a large enough unit cell to accomodate toluene adsorbed parallel to the surface even though the WFC observed seems to support this adsorption geometry. However, for all cases mentioned above the diffraction features are diffuse since the layers were poorly ordered; therefore, caution must be exercized in attempting to deduce much structural information.

## II. Toluene, M-xylene, Mesitylene, T-butylbenzene, and N-butylbenzene Adsorption on the Pt(100)-(5x1) Surface

### A. Work Function Change

The maximum WFC observed on adsorption for these compounds is shown in Table I. The values range from -1.5V for n-butylbenzene and mesitylene to -1.75V for t-butylbenzene. Again, the large amount of electron transfer, the similarity of the WFC on adsorption for the entire series, and the fact that the WFC for mesitylene adsorbed at low pressures is similar to the WFC observed for the other compound in the series indicates that the interaction occurs predominantly between the metal and the π electron cloud of the adsorbate.

The WFC on adsorption of n-butylbenzene depends markedly on the growth rate of the adsorbed overlayer. It appears that this is due to the long side chain which makes reorientation of the adsorbed molecules difficult.

## B. Diffraction Studies

Ordered adsorption on the Pt(100)-(5x1) surface seems to be correlated with the persistance of the (5x1) surface structure for these large π-bonded adsorbates. That is, if the (5x1) surface structure remains detectable after adsorption the adsorbed layer will be fairly well-ordered. On adsorption of toluene, m-xylene, and mesitylene, streaked 1/3 order diffraction features appear which co-exist with the diffraction features due to the (5x1) surface structure. Upon gentle heat treatment, both the (5x1) surface structure and 1/3 order streaks disappear leaving a (1x1) pattern with increased background intensity. On adsorption n-butylbenzene initially causes the appearance of diffuse streaked 1/3 order features along with a decrease in the intensity of the diffraction beams due to the presence of the (5x1) surface structure. With continued exposure both the (5x1) surface structure and the 1/3 order streaks are replaced by a (1x1) pattern with increased background intensity indicating disordered adsorption. T-butylbenzene forms a disordered overlayer on adsorption and the (5x1) surface structure reverts to a (1x1) structure with high background intensity. During this order-disorder transformation in the adsorbed layer while the substrate surface structure is also changing from (5x1) to (1x1), no significant work function change takes place.

Several authors have suggested[9-15] that the (5x1) surface structure may be due to the formation of a hexagonal platinum overlayer on top of the square surface unit cell expected by projecting the bulk structure onto the surface plane. This model explains the observed order-disorder transformation upon changes of substrate structure since a hexagonal surface (even one formed by reconstruction) might be expected to yield more ordered overlayers. It should be noted that several ordered surface structures[1,6] have been observed on the Pt(100)-(1x1) surface even though the (5x1) structure has relaxed. We have observed structures for CO, ethylene acetylene, benzene, and pyridine on the Pt(100)-(1x1) surface structure. These molecules appear to order via the one-step site mechanism. That is, the adsorption occurs with the molecules in a specific orientation at a specific surface site. The bonding arguments made for CO, ethylene and acetylene by other authors[5,16,17] supports this contention. The authors[1] believe that benzene and pyridine interact with the (100) via the formation of an electron pair bond to the Pt(100) surface because of diffraction information and the WFC observed.[1]

During the adsorption of mesitylene at high pressure ($4 \times 10^{-7}$ torr) a pressure induced transition occurs on both low index platinum surfaces. The WFC decreases, and the LEED pattern becomes markedly different (on the Pt(111) a disordered layer forms; on the (100) surface the (5x1) structure converts to (1x1)). A change in the nature of interaction between the substrate and adsorbate is occurring which depends on the incident vapor flux. A comparison with the results obtained for benzene[1] seem to indicate that a $\pi \rightarrow \sigma$ bond transition may be occurring. This may be due to demethylation of the aromatic ring and subsequent interaction with the surface through the demethylated carbon site or dehydrogenation of a methyl group and interaction of the substrate with the dehydrogenated site.

## III. Aniline, Nitrobenzene and Cyanobenzene Adsorption on the Pt(111) Surface

### A. Work Function Change

The WFC observed on adsorption of aniline, nitrobenzene, and cyanobenzene are -1.8V, -1.5V and -1.6V, respectively. The similarity of WFC within the series and also the similarity to the WFC on adsorptions of the other hydrocarbons studied supports the contention that these molecules also interact primarily by forming a $\pi$ bond with the substrate surface. That is, they adsorb with the benzene ring parallel or nearly parallel to the surface. Nitrobenzene appears to decompose in the electron beam when adsorbed on the Pt(111) surface since the WFC and diffraction pattern both change with electron beam exposure at moderate voltages (30V).

### B. Diffraction Studies

The diffraction patterns observed on adsorption are poorly ordered for this group of compounds. All three molecules cause the appearance of 1/3 order features in the diffraction pattern. Aniline adsorption gives rise to streaked diffraction features at 1/3 order along with streaks extending radially to (1/2 0) positions. This diffraction pattern seems to be the result of a poorly ordered complex structure. Adsorption of nitrobenzene and cyanobenzene cause the formation of diffuse 1/3 order diffraction features. Both these molecules,adsorbed with their benzene ring parallel to the metal surface,fit into a (3x3) unit cell. However, the diffraction patterns indicate a greal deal of disorder in the adsorbed layer and the diffuse diffraction features might obscure much information necessary to interpret the surface structures.

## IV. Aniline, Nitrobenzene and Cyanobenzene Adsorption on the Pt(100)-(5x1) Surface

### A. Work Function Change

The WFC's on adsorption of anilene, nitrobenzene and cyanobenzene are -1.75V, -1.4V and -1.5V, respectively. The similarity of the WFC within the series and the similarity to the WFC on adsorption of the other hydrocarbons studied supports the contention that these molecules also interact primarily by forming a π bond with the substrate surface. We expect the molecules to be adsorbed with their benzene ring parallel or nearly parallel to the substrate surface. Nitrobenzene adsorbed on the Pt(100)-(5x1) surface is not as sensitive to electron beam exposure as the overlayer on the Pt(111) surface. Apparently small changes in the interaction between substrate and adsorbate can markedly affect the electron beam sensitivity of the adsorbed layer.

### B. Diffraction Studies

These compounds form disordered overlayers on adsorption.

## Summary

The substituted aromatic molecules studied interact with the metal surface by forming $\pi$ bonds. They form ordered layers via a two-step mechanism involving disordered initial adsorption and subsequent reorientation and ordering. The shape of the molecules determines the ease of reorientation. Molecules with high rotational symmetry or small substituents reorient more easily and form more ordered overlayers on the platinum substrate with higher rotational symmetry [Pt(111)].

## Acknowledgement

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