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Author
Lin, R.F.

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R. F. Lin, R. J. Koestner, M. A. Van Hove and G. A. Somorjai
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and Department of Chemistry
University of California
Berkeley, CA 94720

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R. F. Lin, R. J. Koestner, M. A. Van Hove and G. A. Somorjai
Materials and Molecular Research Division
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ABSTRACT

The adsorption of benzene and naphthalene on the Rh(111) single-crystal surface has been studied by low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) and thermal desorption spectroscopy (TDS). Both benzene and naphthalene form two different ordered surface structures separated by temperature-induced phase transitions: benzene transforms from a \(\frac{31}{13}\) structure, which can also be labelled \(c(2\sqrt{3}x4)\)rect, to a \(3x3\) structure in the range of 363-395K, while naphthalene, transforms from a \(3\sqrt{3}x3\sqrt{3}\)R30° structure to a \(3x3\) structure in the range 398-423K. Increasing the temperature further, these structures are found to disorder at about 393K for benzene and about 448K for naphthalene. Then, a first \(H_2\) desorption peak appears at about 413K for benzene and 578K for naphthalene and is interpreted as due to the occurrence of molecular dissociation. All these phase transitions are irreversible. The ordered structures are interpreted as due to flat-lying or nearly flat-lying intact molecules on the rhodium surface, and they are compared with similar structures found on other metal surfaces. Structural models and phase transition mechanisms are proposed.
1. Introduction

The structure and bonding of aromatic and cyclic organic molecules on transition metal surfaces is of great interest in surface science, especially when applied to studies of adhesion, lubrication and heterogeneous catalysis. In the past few years, several papers have dealt with monolayers of aromatic molecules adsorbed on Pt, Ni, Pd and other metal surfaces.\cite{1-10} Most of the reports were concerned with benzene (C\textsubscript{6}H\textsubscript{6}),\cite{1-7} while others dealt with naphthalene (C\textsubscript{8}H\textsubscript{10}) and azulene (also C\textsubscript{8}H\textsubscript{10}, but with a 5- and a 7-carbon ring, rather than two 6-carbon rings as for naphthalene).\cite{8-10}

Demuth and Eastman\cite{11} compared the ultraviolet photoelectron spectroscopy (UPS) results of benzene adsorbed on the Ni(111) single-crystal surface at temperatures between 100 and 300K with self-consistent-field/linear-combination-of-atomic-orbital (SCF/LCAO) calculations; they concluded that the benzene molecule should be predominantly π-bonded on the metal surface and therefore that the benzene ring should lie parallel to the surface. Bertolini et al.\cite{5} and Lehwald et al.\cite{6} reached the same conclusion in high-resolution electron energy loss spectroscopy (HREELS) studies of benzene adsorption on Pt and Ni surfaces. Gland and Somorjai\cite{12} and Stair and Somorjai\cite{7} carried out low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) and work function change studies of benzene adsorbed on Pt(111). They found that benzene undergoes a change of structure with increasing coverage, which is associated with a large change of work function. Tsai and Muetterties have studied
the thermal desorption spectroscopy (TDS) of benzene and related molecules on Pt(111).\textsuperscript{[13]}

The surface structure of naphthalene was studied by Gland and Somorjai\textsuperscript{[12]} and Firment and Somorjai\textsuperscript{[14]} on Pt(111) using LEED. They found a (6x3) ordered structure with two symmetry planes. Dahlgren and Hemminger\textsuperscript{[10]} investigated the ordering of azulene and naphthalene adsorbed on Pt(111) as a function of temperature in the range 273-473K. Their structural results have been compared with force-field calculations of the optimum structure by Gavezzotti and Simonetta.\textsuperscript{[15]}

All of these structural studies of aromatic molecules on metal surfaces are still attempting to determine the adsorption site and the tilt angle, if any, of the carbon rings relative to the surface plane.

In this paper we describe LEED, AES and TDS studies of benzene and naphthalene adsorbed on the Rh(111) crystal surface. Two different ordered phases have been found for each of these molecules and the phase transitions have been investigated. These results, when compared with adsorption studies of the same molecules on other metal surfaces, can be used to obtain insight into the nature of the chemical bond and the structure of these aromatic molecules on metal surfaces.

2. \textbf{Experiment}

The ultra-high vacuum (UHV) chamber was maintained at a 5 to $10 \times 10^{-10}$ torr base pressure during the adsorption experiments by using a 200 liter/sec ion pump and a water-cooled titanium sublimation pump.
The chamber is equipped with four-grid LEED/Auger optics, an ion sputtering gun and a quadrupole mass spectrometer. A glancing-incidence electron gun is also mounted on the chamber for use in Auger Electron Spectroscopy. Mu metal shielding is wrapped cylindrically around the LEED gun and sample to avoid deflection of the low-energy electrons by external magnetic fields.

The rhodium single crystal sample (~1 cm diameter disk of (111) orientation within ±0.5°) is spot welded onto a 4 mil Ta foil and can be heated resistively to 1475K. The sample can also be cooled to 220K by immersing the copper bars, which are thermally attached to the sample via copper braids, in liquid nitrogen. The Rh single crystal samples were oriented and spark cut to the (111) plane, then polished with a sequence of finer emery grits and finally with a 0.5 μm diamond paste.

The Rh samples contained small amounts of sulfur, chlorine and carbon impurities as well as greater amounts of boron. A combination of Ar⁺ bombardment and oxygen treatments were used for cleaning. In our experiments, two weeks of continuous Ar⁺ bombardments (1 to 3 μA at 1.2 kV) coupled with periodic 5 min annealing cycles at 1075K and O₂ treatments (flowing 5x10⁻⁷ torr O₂ at 975K) was needed to deplete boron from the near-surface region.

The benzene and naphthalene used in our experiments were reagent grade. They were stored in a glass vessel which was connected to a stainless steel manifold (the use of copper tubings was avoided as it may facilitate the decomposition of naphthalene); the glass was sealed to the metal with a torr seal connector using viton gaskets. The
manifold was baked at 355 to 375K for a few hours with the ion pump, before the organic vapor was introduced into the line. The benzene and naphthalene samples were degassed by three freeze-pump-thaw cycles prior to every adsorption experiment. With this treatment the manifold pressure was less than $5 \times 10^{-3}$ torr when the benzene or naphthalene was cooled down to a liquid nitrogen temperature and the pumps (both sorption and ion) were valved off. The manifold was then filled with the benzene or naphthalene vapor just prior to the adsorption experiment. The vapor pressure of benzene in the manifold was ~100 torr at room temperature. Naphthalene had to be melted at 355K to obtain a sufficiently high vapor pressure and the manifold was kept at 355K to maintain its partial pressure at 20 torr at the leak valve. The vacuum side of the leak valve was not heated directly and the naphthalene was introduced into the chamber by a 3" x 1/4" O.D. and 1" x 1/16" O.D. stainless steel tube near the crystal.

The photographic technique [7] was used to collect all the LEED intensity vs. voltage curves. In this method, photographs of the LEED pattern displayed on the fluorescent screen are taken at 2eV intervals. A computer controlled stepping microdensitometer is used to scan the processed film and the digital output is stored on a magnetic tape. A set of computer programs is then used to determine the intensity of each diffraction spot and to produce I-V curves, which are normalized for constant incident beam current.
3. Results and Discussion of the Surface Structure of Benzene Adsorption on Rh(111)

3.1 Results for benzene adsorption on Rh(111)

A well ordered benzene monolayer was formed on the Rh(111) surface at 238K upon a 30L (1 Langmuir=1 torr. sec) exposure of benzene (all exposure levels are uncorrected for variations of ion gauge sensitivity or the pressure difference between the gauge and the sample). When a 70L exposure was used, annealing of the sample at 348K for 5 min was necessary to form a well-ordered commensurate overlayer, whose LEED pattern is shown in Fig. 1a, together with the corresponding real-space surface unit cell in Fig. 1b. In the matrix notation, that relates a superlattice to the two-dimensional substrate lattice, this structure can be labelled \( \frac{31}{13} \); in a new notation, [16] that often helps to visualize the structure more readily with the help of a rectangular unit cell, this structure can also be labelled \( c(2\sqrt{3} \times 4)_{\text{rect}} \), meaning that the unit cell is a centered rectangle with sides of lengths \( 2\sqrt{3} \) and 4 in terms of the side of the (1x1) substrate unit cell. Three rotated domains of this superlattice are needed to explain the observed pattern in accordance with the threefold rotational symmetry of the substrate surface.

This \( \frac{31}{13} \) structure was stable up to 358K. Above 363K it began to transform into another ordered structure. After heating the sample at 373K for 15 min, a well-ordered \( (3x3) = \frac{30}{03} \) structure appeared. Figure 2a displays the LEED pattern and Fig. 2b shows the real-space unit cell for the \((3x3)\) structure. A mixed phase that
contains domains of both the (3\textsubscript{13}) and (3x3) surface structures could be produced by long annealing (60 min) at 363K, the pattern for which is shown in Fig. 3. However, the (3\textsubscript{13}) $\rightarrow$ (3x3) phase transition occurred at a higher temperature (~395K) during a rapid flash (10 K/sec) of the sample. Continued heating of the (3x3) structure at 393K for 3 min caused it to disorder. Both of these phase transitions, from (3\textsubscript{13}) to (3x3) and from (3x3) to disordered, are irreversible processes. Our AES measurements showed no detectable difference in the carbon coverage of the rhodium surface in the (3\textsubscript{13}) or (3x3) structures, but the relative accuracy of these measurements is at best about 10 percent.

The thermal desorption spectra of H\textsubscript{2} from the (3\textsubscript{13}) and (3x3) benzene overlayers on Rh(111) are indistinguishable: they are shown in Fig. 4. The desorption was produced by a linear temperature ramp of 10K/sec (which is the same ramp used in the flash that produced a (3\textsubscript{13}) $\rightarrow$ (3x3) phase transition at about 395K). The first desorption peak occurs at 413K and a second, broader peak appears at 563K. Hydrogen must come from the decomposition of the benzene molecules and from the subsequent dehydrogenation of the remaining hydrocarbon fragments, because any atomic hydrogen adsorbed directly on the metal surface would have desorbed at much lower temperatures. [17]

We have in addition measured a set of LEED I-V curves at three angles of incidence (\(\phi = 0^\circ, 10^\circ\) and \(20^\circ\)): some of these will be discussed and shown in connection with corresponding naphthalene I-V curves in Section 4.
3.2 Discussion of benzene structures on the Rh(111) surface

Our TDS data indicate that the benzene molecules in the \((31\overline{1})\) structure are intact until the transition to the \((3\times3)\) structure starts. HREELS experiments [18] indicate that the benzene molecules in the \((31\overline{1})\) surface structure or Rh(111) not only are intact, but also lie flat above the metal surface. In all other HREELS experiments with benzene adsorbed on different metal surfaces [5,6], the benzene ring also appears to lie parallel to the substrate surface. And TDS work [13] performed on Pt(111) further implies flat-lying molecules.

Several attempts have been made by HREELS to determine the adsorption site (registry) and azimuthal orientation (about the surface normal) of benzene on these metal surfaces. However, because of the uncertainties of interpretation we shall consider the site and orientation to be unsettled (LEED I-V curve analyses of the benzene surface structures are in progress in our laboratory to resolve these questions). Another argument in favor of flat-lying benzene molecules is the fact that the Van der Waals size of the benzene molecule is quite compatible with flat-lying positions of the benzene in the \((31\overline{1})\) and \((3\times3)\) structures on Rh(111), if one assumes that exactly one molecule fits in each unit cell. Some possible models are shown in Figs. 1c and 1d, and in Figs. 2c and 2d, respectively. The benzene centers have been arbitrarily positioned over top sites of the substrate, and two choices of azimuthal orientation with relatively high symmetry are displayed; hollow, bridge and even less symmetrical sites are also possible, as well as orientations that yield lower symmetry.
In the \((\frac{31}{13})\) structure shown in Fig. 1, the smallest intermolecular H-H distances are 2.9 and 3.0\(\text{Å}\) for Fig. 1c, and 2.4\(\text{Å}\) for Fig. 1d (assuming Rh-Rh, C-C and C-H bond lengths of 2.68, 1.395 and 1.1\(\text{Å}\), respectively). In three-dimensional hydrocarbon crystals, the corresponding Van der Waals distances are typically 2.2 to 2.4\(\text{Å}\) [19]; thus, the \((\frac{31}{13})\) structure provides an efficient packing of benzene molecules on the Rh(111) surface. In the \((3x3)\) structure shown in Fig. 2, the H-H distances are larger: 3.1\(\text{Å}\) in Fig. 2c and 3.7\(\text{Å}\) in Fig. 2d. This enlargement corresponds to a lower benzene density in the \((3x3)\) compared to the \((\frac{31}{13})\) structure: the ratio of the areas of the superlattice unit cell and the \((1x1)\) substrate unit cell is \(\text{det}(\frac{31}{13}) = 8\) in the \((\frac{31}{13})\) case, and \(3x3 = 9\) in the \((3x3)\) case, i.e., one molecule "covers" 8 Rh atoms in the \((\frac{31}{13})\) structure and 9 Rh atoms in the \((3x3)\) structure. The corresponding benzene (and carbon) coverages for the two structures are thus in a ratio of 9 to 8, which is compatible with the AES observations of approximately constant carbon coverage within the experimental uncertainty.

Ordered structures of adsorbed benzene have been observed on several metal surfaces: it is significant that they are all compatible with flat-lying benzene molecules, as we shall now show. The area of the benzene molecule in projection on its ring plane can be roughly estimated as that of the smallest rectangle that encloses it, using the Van der Waals radii of 1.2\(\text{Å}\): 50\(\text{Å}^2\). In the following cases the observed LEED pattern is consistent with one molecule per unit cell (the unit cell area \(A\) is given for comparison).
Ni(100) c(4x4)-C₆H₆[6], \quad A = 49.60Å²,
Rh(111)(31/13)-C₆H₆, \quad A = 49.76Å²,
Rh(111)(3x3)-C₆H₆, \quad A = 55.98Å²,
Ir(111)(3x3)-C₆H₆[20], \quad A = 57.66Å²,
Pd(100)C(4x4)-C₆H₆[2], \quad A = 60.06Å²,
Ni(111)(2√3 x 2√3)R30°-C₆H₆[6], \quad A = 64.43Å².

On Pt(111) two benzene patterns have been observed, that may be explained in terms of two flat-lying molecules per unit cell (half the unit cell area is therefore given here):

Pt(111)(2√3 x 4)rect-2C₆H₆[7], \quad A/2 = 53.16Å²,
Pt(111)(2√3 x 5)rect-2C₆H₆[7], \quad A/2 = 66.45Å².

It is of interest that no well-ordered incommensurate benzene structures have been reported in the literature or observed in our work on the various metal surfaces: this may imply that the substrate-benzene interactions are strong compared with the benzene-benzene interactions.

One notices also that only certain LEED patterns arise, but no others which a priori would seem equally compatible with the known size and shape of the benzene molecule. In Fig. 5 we represent the various two-dimensional commensurate superlattices that have unit cell areas and shapes roughly compatible with those of flat-lying benzene. Table 1 shows corresponding unit cell areas on individual metal surfaces, taking the metal lattice constant into account (it is useful
to remember that the unit cell areas are simply proportional to the determinant of the matrix used in the matrix notation for super-
lattices). Which of these unit cells could exist on a given metal
surface clearly depends on the particular metal lattice constant and
the detailed assumptions one makes about the benzene size and shape.
We shall assume an undistorted benzene molecule with Van der Waals
spheres of 1.2Å radius about each hydrogen nucleus and we shall
restrict ourselves to unit cell areas that fall approximately within
the range of the observed ones, namely between 48Å² and 68Å² (see
underlined sizes in Table 1): this defines a collection of "acceptable"
unit cells.

The following among these acceptable structures have not been
reported or observed experimentally:

(3x3), (30), (22), (31) and (32) on Ni(100),
13 13 13 22

(3x3), (30), (22), and (31) on Pd(100),
13 13 12

(33), (22), and perhaps (33) and (3x3) on Ni(111)
12 23 12

(22) and (33) on Rh(111),
23 12

(22), (33) and (31) on Ir(111),
23 12 13

(22), (33), and (3x3) and (31) on Pt(111).
23 12 13

It may be that additional constraints restrict the possible structural
arrangements. For example, the molecular shape may change somewhat
upon adsorption, in different ways on different metals. Or the bonding
mechanism to the substrate may favor some unit cells over others.
It can be seen in Table 1 that the area of those observed unit cells which contain one molecule between about $48\text{Å}^2$ and $68\text{Å}^2$. The lower limit represents the onset of strong repulsion between neighboring benzene molecules at close separations, while the upper limit presumably corresponds to the loss of attraction between neighboring molecules at larger separations.

3.3 Benzene phase transitions on Rh(111)

To propose a model for the $\frac{31}{13} \rightarrow (3\times3)$ phase transition, we start with the fact that, in principle at least, the benzene coverage must decrease by a factor 8/9 due to the change in unit cell area. This reduction can come either from decomposition or from desorption of benzene molecules. We favor the decomposition of benzene molecules as a main cause of the phase transition for the following reasons:

1. Decomposition would leave the carbon coverage (as opposed to benzene coverage) unchanged, in agreement with the AES measurements;

2. the irreversibility of the phase transition can be easily explained by partial decomposition; [3] the phase transition occurs at 363 to 395 K, which is reasonably close to the decomposition temperature (~413K) of benzene molecules on the Rh(111) surface, corresponding to the first peak in the $H_2$ thermal desorption spectrum from benzene. This phase transition model suggests that the (3x3) structure is stabilized by carbon impurities. There is further evidence to support this suggestion of impurity-stabilization: (1) In our initial experiments, in which some sulfur and carbon impurities were present on the surface, we could only form the (3x3) structure; (2) The benzene
phase transition from $(2\sqrt{3} \times 4)$rect to $(2\sqrt{3} \times 5)$rect on Pt(111) also was favored by the presence of carbon impurities. Thus, we propose that a limited amount of benzene decomposition occurs near or below the $(31 \over 13) \rightarrow (3 \times 3)$ phase transition on Rh(111) (with only little hydrogen evolution as detected by TDS) and that this decomposition favors the phase transition while making it irreversible.

An advantage of this decomposition model is that we can also use it to explain the phase transition observed for benzene on Pt(111) [7], which has been mentioned above, but for which no satisfactory mechanism has yet been proposed. For example, the decomposition model would make the large work function change plausible, which was observed during the transition [7]: the decomposed atomic carbon or other fragments could produce the necessary large charge transfer.

It also becomes possible to propose a detailed geometry for the $(2\sqrt{3} \times 4)$rect and $(2\sqrt{3} \times 5)$rect structures on Pt(111), shown in Fig. 6, if we use in addition our detection of spot extinctions in the LEED patterns that were photographed previously [7] for these structures on Pt(111), which reveal the existence of glide planes. We assume that two benzene molecules fit flat in each unit cell, and that bridge sitting of the molecular centers is favored. The bridge site is used as it leads most naturally to the observed glide plane symmetries (our terminology for adsorption sites refers to the molecular center). At the same time, this adsorption site allows reasonable intermolecular distances in both $(2\sqrt{3} \times 4)$rect and $(2\sqrt{3} \times 5)$rect, because of the added freedom of using differently oriented bridge sites, which is not present with higher-symmetry sites like top or three-fold hollow.
It is furthermore possible to allow within our model, under all circumstances, and on any substrate, a mixture of ordered molecules and carbon in the form of decomposition fragments: only part of the surface would consist of well-ordered molecules, while the rest could be a disordered layer of carbon atoms and other molecular fragments of the type $C_xH_y$. This could explain the relatively high carbon coverage detected in the adsorption structures of benzene on Pt(111) [7].

Finally, we may compare the positions of the first $H_2$ desorption peak for benzene adsorbed on Rh(111) (at 413K), on Ni(111) (at 453K) and on Pt(111) (at 443K): it is clear that the decomposition of benzene molecules occurs at a lower temperature on the Rh(111) surface. Thus, the C-H bond scission is more facile on the Rh(111) surface than on the Ni(111) and Pt(111) surfaces.

4. Results and Discussion of the Surface Structure of Naphthalene Adsorption on Rh(111)

4.1 Results for Naphthalene Adsorption on Rh(111)

When the clean Rh(111) crystal surface was exposed to 5L of naphthalene at a sample temperature of 233K, an overlayer with a poorly ordered (3x3) structure formed. By annealing the sample at 348K for 5 minutes, a clear LEED pattern appeared, shown in Figs. 7a and 7b, which corresponds to a surface structure that may be labelled $(3\sqrt{3}x3\sqrt{3})R30^\circ$, which is equivalent to $(\frac{63}{36})$. The third-order diffraction spots in this pattern were much more intense than the other fractional-order spots at all incident energies.
By heating the sample at 398-423K for 5 minutes, this ordered overlayer changed to a well-ordered (3x3) structure with faint background, whose LEED pattern is shown in Fig. 8a. Upon further heating the sample to 448K for 5 minutes, the naphthalene overlayer disordered permanently. Attempts to reverse the phase transitions were largely unsuccessful. The only exception was a partial (3x3) to $(3\sqrt{3}x3\sqrt{3})R30^\circ$ transition that could be detected under prolonged electron beam irradiation.

The results of AES measurements suggest that the carbon coverages in the two ordered naphthalene structures described above are essentially the same.

The $H_2$ desorption spectrum from adsorbed naphthalene on Rh(111) is shown in Fig. 9. The first sharp peak occurs near 578K and the second broader peak is at 698K. A linear temperature ramp of 10K/sec was used to obtain this spectrum. The first peak is due to the decomposition of naphthalene molecules and the second, high-temperature peak comes from the further dehydrogenation of hydrocarbon fragments.

We have also measured intensity vs. energy profiles (I-V curves) for a number of beams of the naphthalene structures. We chose the same set of measurement conditions as with the benzene structures, namely incidence angles of $\theta = 0^\circ$, 10° and 20°. There appear many similarities between equivalent beams of the (3x3) type (i.e., third-order beams) for different structures of naphthalene and benzene: these are shown in Fig. 10 and will be examined in the discussion.
4.2 Discussion of naphthalene structures on the Rh(111) surface

We first note that the area of the (3x3) unit cell on Rh(111) is quite comparable with that of a flat-lying naphthalene molecule with its Van der Waals dimensions, as is illustrated in Figure 8c (even though the molecular shape is not very well suited to the unit cell shape). A (3√3x 3√3)R30° unit cell has an area exactly three times that of a (3x3) unit cell, so that one can imagine three naphthalene molecules to lie flat inside such a cell.

We must now consider whether the observed (3√3 x 3√3)R30° LEED pattern corresponds simply to a (3√3x 3√3)R30° structure or to a combination of different domains with different unit cells. We have discounted the possibility that differently oriented domains of (3√3x3√3)R30° occur in conjunction with a (3x3) structure (the coexistence of (3x3) domains would be needed to explain the presence of certain third-order spots). A serious drawback for this model is that the (3√3x3√3)R30° lattice would generate particularly much intensity in the (√3·√3)R30°-like extra spots (because relatively more domains would contribute to those spots), in contrast to the experimental evidence. The (3√3·√3)R30° unit cell does have an area that is appropriate for a flat-lying naphthalene molecule (namely equal to that of a (3x3) unit cell), but its shape is not suitable: the excessive length of the cell leaves free space at the ends of the molecule, while its narrowness would have to be explained by tilting the molecule around its long axis away from parallelism with the surface.
A more likely interpretation of the observed pattern, with its intense (3x3)-like spots, is the coexistence of a $(3\sqrt{3}\times 3\sqrt{3})R30^\circ$ lattice with a (3x3) lattice, which we shall call the "superposition model". This is especially attractive because the higher-temperature phase of naphthalene on Rh(111) shows a pure (3x3) pattern. But this suggests yet another possibility: we may have a (3x3) arrangement of molecules with a superimposed modulation or other modification in which a strong similarity with the (3x3) arrangement is kept, while a $(3\sqrt{3}\times 3\sqrt{3})R30^\circ$ periodicity is adopted. This modulation or modification would then simply become disordered or otherwise disappear after going through the phase transition to the (3x3) structure. The possibility of such a modulation is supported by the difficulty of fitting an undistorted naphthalene molecule flat on the surface within the (3x3) unit cell, cf. Fig. 8c: there is too much overlap between neighboring molecules in comparison with the standard Van der Waals radii. The optimum arrangement in a (3x3) lattice occurs when the molecules in Fig. 8c are rotated together away from the drawn orientation by $-20^\circ$ about the surface normal, as then the smallest intermolecular H-H distance becomes $\sim 1.75\text{Å}$, still much smaller than the desired 2.4Å. Therefore, some differential tilting, rotation or other rigid change of the positions of the naphthalene molecules with respect to each other is likely, which implies a unit cell containing more than one molecule and larger than (3x3). One model involving only rotations about the surface normal of flat-lying molecules is shown in Fig. 11. Remember that the area of the $(3\sqrt{3}\times 3\sqrt{3})R30^\circ$ cell is
compatible with the presence of three flat-lying naphthalene molecules, so that the coverage is the same as in the (3x3) arrangement with one molecule per unit cell.

We may compare the structures observed for naphthalene on Rh(111) with those obtained on Pt(111) for the same molecule and its azulene isomer (which has a 5- and a 7-carbon ring as opposed to the two 6-carbon rings of naphthalene). Naphthalene on Pt(111) adopts [9] a (6x3) unit cell with glide plane symmetry that most likely contains two flat-lying molecules. Force-field calculations have confirmed[15] that such a geometry is energetically favorable. Azulene on Pt(111) takes on various structures,[8] including a (3x3) structure and an incommensurate structure labelled (3x3)R30°: these again appear to be compatible with flat-lying molecules and undergo phase transitions that are similar to those that we encountered for benzene and naphthalene on Rh(111).

In terms of area occupied by the adsorbed molecules, the (6x3) naphthalene unit cell, if it contains two molecules, yields an occupied surface area of 59.8Å² per molecule on Pt(111), while the (3x3) unit cell with one molecule and the (3√3x3√3)R30° unit cell with three molecules both yield 55.98Å² per molecule on Rh(111).

An important piece of structural evidence for naphthalene on Rh(111) is the close similarity of the I-V curves for the (3x3)-like spots between the (3√3x3√3)R30° and the (3x3) structures, cf. Fig. 10. Should the low-temperature phase be the superposition model with an uneven mixture of some (3√3x3√3)R30° domains and many (3x3) domains, giving strong (3x3) spots, then this similarity is not
surprising and it indicates that the (3x3) domains do not change appreciably during the phase transition. If we have the superposition model with more even domain sizes or, on the other hand, if the \((3√\text{3}×3\sqrt{3})\text{R}30°\) structure is a modulated or modified (3x3) structure, then this I-V curve similarity gives more subtle information: there is clearly a structural difference (since the unit cells are different), but the position of the molecules with respect to the substrate can be said to be essentially the same in the two structures. This is because the energy structure of the I-V curves is mostly affected by the short-range order of surfaces, as opposed to the long-range order. In other words, if two surface structures have the same short-range structure (e.g., identical molecular binding sites) but different unit cell dimensions, any beams common to both structures will have similar I-V curves. This is a recent realization that needs further exploration and explanation, but it has already been established both with experiments [21] and with model calculations [21,22]. We now describe this principle in the special case of naphthalene.

An example of different but very similar structures is provided by comparing the (3x3) arrangement of flat-lying naphthalene molecules shown in Fig. 8 with the \((3√\text{3}×3\sqrt{3})\text{R}30°\) arrangement obtained by molecular rotations, as shown in Fig. 11. The (3x3) arrangement allows three symmetry-equivalent rotated domains. Each rotated domain matches one of the three molecular orientations present in the \((3√\text{3}×3\sqrt{3})\text{R}30°\) model. Thus, in both structures, each of the three molecular orientations is present in equal proportions. The difference from the
standpoint of diffraction consists in the following: if molecules with
different orientations are distant from each other, as in the (3x3)
case, where they must belong to different domains, they scatter without
interference (addition of diffracted intensities); if these molecules
are close together, as in the (3√3x3√3)R30° case, they scatter with
interference (addition of complex amplitudes). This difference shows
up in I-V curves mainly if multiple scattering between neighboring
molecules is appreciable; this is however only expected with very dense
overlayers (e.g., metallic monolayers), so that we can understand the
similarity of I-V curves with our proposed models of Figs. 8 and 11.

With other examples, the argument for similarity of I-V curves
might have to be different. Thus, if we modulate the (3x3) structure
not by the above rotations, but by various small tilts of the molecules
away from parallelism with the surface, we must argue that the tilts
are small enough not to affect the intensities of the (3x3)-like spots,
while being large enough to generate the other fractional-order spots.
We cannot use quantitative arguments here in determining the degree of
I-V curve similarity that one expects from rotations or small tilts;
model calculations have to be performed for that purpose, which are
planned. In a general sense, the issue of what is implied by I-V
curves similarities is quite important: once it is understood, one can
draw direct conclusions about different structures that produce similar
experimental I-V curves. Such an understanding would allow one to
reach detailed structural conclusions without calculating I-V curves,
but by direct comparison with measured I-V curves for another structure
that is already known. Such an understanding is lacking at present, however.

An other intriguing I-V curve similarity is evident when one compares corresponding I-V curves for the naphthalene and benzene structures, cf. Fig. 10. Unfortunately, only a few beams are available at present for this comparison. Model calculations\textsuperscript{[22]} have shown similarities of this kind in I-V curves for benzene vs. naphthalene adsorption in equivalent sites (i.e., naphthalene is obtained by adding four carbon atoms to a benzene ring, whose registry is not changed). However, our present data base is not sufficient to draw conclusions at this point.

4.3 Naphthalene phase transitions

In Section 3, we proposed that partial molecular decomposition may be responsible for the irreversible benzene phase transition on Rh(111). That mechanism is especially plausible as the first $H_2$ thermal desorption peak occurs at a temperature that is only slightly higher than the phase transition temperature. In the case of naphthalene, there is a much larger temperature difference (~150K vs. at most ~30K for benzene) between the irreversible phase transition and the decomposition. To invoke the decomposition as the cause for the transition therefore requires some additional argument. Possibilities are low-temperature partial decomposition of naphthalene with $H_2$ production; or the need for only a very small amount of decomposition to trigger the transition; or the segregation of bulk impurities to the surface, which would trigger the transition; or the coadsorption of CO...
or \( O_2 \) (coadsorption of CO or \( O_2 \) from the gas phase is made more likely by some evidence for desorption of naphthalene: the pressure in the chamber increased when the sample was heated through the phase transition).

5. **Summary**

(i) We have observed two different ordered structures for benzene and naphthalene monolayers adsorbed on the Rh(111) single-crystal surface, namely: for benzene, a \((3113) = c(2\sqrt{3}x4)\text{rect} \) and a \((3x3)\) surface structure (see also Ref. 21); for naphthalene, a \((3\sqrt{3}x3\sqrt{3})\text{R}30^\circ \) and a \((3x3)\) surface structure.

(ii) The two benzene structures on Rh(111) are compatible with flat-lying molecules at two slightly different surface coverages. They also compare favorably with a number of ordered benzene structures observed on other metal substrates.

(iii) The two naphthalene structures on Rh(111) are closely related to each other, as evidenced by very similar I-V curves. Their detailed structures may involve differential tilts or rotations, i.e., the molecules may not be quite parallel to each other.

(iv) The order-order phase transitions occur at about 373K and 423K for benzene and naphthalene, respectively, and they are both irreversible processes. There are also order-disorder phase transitions at 393K and 448K, respectively. All of
these phase transitions occur below or near the first hydrogen TDS peaks. There is evidence that the high-temperature ordered phase may be stabilized by the presence of segregated bulk impurities or of carbonaceous fragments from the partially decomposed molecules.

Acknowledgements

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References


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be published
Table 1. Superlattice unit cell areas on various substrates in multiples of the (1x1) substrate unit cell area. For example, the area of a (3x3) unit cell can be found in the column labelled 9x. Double-underlined are unit cell areas that have been observed for benzene adsorption. Single-underlined are unit cell areas that have not been observed, but are plausible on the basis of the observed ones. (In the case of Pt(111) the double-underlined values are half the observed unit cell areas, since two benzene molecules are presumed to fit in the observed unit cells.)

<table>
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<th>Substrate</th>
<th>6x</th>
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<th>8x</th>
<th>9x</th>
<th>10x</th>
<th>11x</th>
<th>12x</th>
<th>13x</th>
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<td>68.20</td>
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<td>74.64</td>
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Figure Captions

Fig. 1. \( \text{Rh}(111) \frac{31}{13} - C_6H_6 \) (benzene). (a) LEED pattern at normal incidence at beam energy 50 eV: diffraction photograph at left; schematic diagram at right showing three unit cells in reciprocal space, corresponding to three domain orientations. (b) Real-space unit cell corresponding to the observed diffraction pattern, exhibiting the \( \frac{31}{13} \) unit cell and the centered rectangular \( c(2\sqrt{3}x4) \) rect cell for one domain orientation. (c) and (d) Two possible models for benzene adsorption, differing by the azimuthal orientation of flat-lying molecules. The molecules are drawn as lines connecting C and H nuclei. The closest intermolecular distances are shown between H nuclei.

Fig. 2. \( \text{Rh}(111) \ (3x3) - C_6H_6 \) (benzene). (a) Photograph of LEED pattern at normal incidence at beam energy 50eV. (b) Real-space unit cell corresponding to the observed pattern. (c) and (d) Two possible models for benzene adsorption, analogous to Figures 1c and 1d.

Fig. 3. Photograph of mixed \( \frac{31}{13} + (3x3) \) LEED pattern observed for benzene adsorbed on Rh(111).

Fig. 4. \( \text{H}_2 \) thermal desorption spectrum from benzene adsorbed on Rh(111) in both the \( \frac{31}{13} \) and the (3x3) structures.

Fig. 5. Superlattice unit cells on fcc(111) and (100) metal surfaces, that have a size and shape comparable to that of one flat-lying benzene molecule per cell (but two molecules per
cell in the case of the \((2\sqrt{3} \times 4)\text{rect}\) and \((2\sqrt{3} \times 5)\text{rect}\) superlattices). The experimentally observed unit cells are drawn in heavy lines. The unit cell area is given as "nx" (n integer), i.e., a multiple of the \((1\times 1)\) substrate unit cell area, which notation refers to the column headings of Table 1.

**Fig. 6.** Proposed model for benzene on Pt(111) in \((2\sqrt{3} \times 4)\text{rect}\) and \((2\sqrt{3} \times 5)\text{rect}\) arrangements, assuming two flat-lying molecules per unit cell and bridge sites for the molecular centers.

**Fig. 7.** Rh(111) \((3\sqrt{3} \times 3 \sqrt{3})\text{R}30^\circ-C_{10}H_8\) (naphthalene).
(a) Photograph of LEED pattern at beam energy 50eV (at left) and schematic indicating the \((3\times 3)\) array of intense spots (at right). (b) Real-space unit cell corresponding to the observed pattern.

**Fig. 8.** Rh(111) \((3\times 3)-C_{10}H_8\) (naphthalene). (a) Photograph of LEED pattern at normal incidence at beam energy 50eV. (b) Real-space unit cell corresponding to the observed pattern.
(c) A least-overlap model for flat-lying naphthalene molecules in a \((3\times 3)\) arrangement, exhibiting the impossibility of totally removing the overlap between neighboring molecules.

**Fig. 9.** H\(_2\) thermal desorption spectrum from naphthalene adsorbed on Rh(111) in the \((3\times 3)\) structure.

**Fig. 10.** Measured I-V curves for \((3\times 3)\)-like spots (i.e., third-order spots), for two different structures of naphthalene and one structure of benzene adsorbed on Rh(111). The intensities
were recorded at normal incidence and with a sample
temperature of 240K. The intensities are normalized to a
constant maximum intensity for all curves.

Fig. 11. A model for Rh(111) (3√3x3√3)R30°-C_{10}H_{8} with three
naphthalene molecules per unit cell, which lie flat and do
not overlap.
Figure 2

(3x3)
(Implied coverage, $\theta_c = 2/3$)

(a)

(b)

(c) 3.1 Å

(d) 3.7 Å
Figure 4
Rh(III) - C$_{10}$ H$_8$

(3 x 3)

Figure 8
Figure 9

\[ P_{H_2} \text{ (arb. units)} \]

\[ \text{Rh(III)}-(3\times3)-C_{10}H_8 \quad 578K \]

Disordered (3x3)

(3\sqrt{3} \times 3\sqrt{3})

R 30°

300 400 500 600 700

T (K)
Figure 10
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