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Benzene on Pd(110): The first example of nonparallel adsorption

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In contrast with previously reported examples of benzene chemisorbed on metal surfaces with parallel orientation, adsorption of a Pd(110) surface appears to produce a tilted ring. Polarized light angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) experiments in the mirror planes of the surface show that the adsorbate spectra give the expected strong polarization effects in the [001] azimuth but not in the [1$\bar{1}$0] azimuth. The azimuthal orientation of the ring is determined, and a tilt of the molecule of the order of 10°–20° into the grooves of the surface, towards [001] is proposed, so that the overall symmetry is reduced to C_s. A sharp $c(4\times2)$ low-energy electron-diffraction (LEED) pattern is observed. The azimuthal orientation and the tilt determined from ARUPS are those required to minimize steric interactions in a model for the LEED pattern.

Angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) using polarized synchrotron radiation is a powerful technique for the study of the symmetry properties of molecules at surfaces. The electron current photoemitted from the molecular moiety into high-symmetry directions can be predicted from polarization-dependent selection rules. These are related to the point-group symmetry of the adsorption complex, and can be derived from the symmetry properties of a dipolar transition-matrix element by application of simple group theory.[1-3] Accordingly, the symmetry of the adsorption complex can be determined, and with a suitable model the structure and orientation of the adsorbed molecule can be established. In the present Rapid Communication, we report the application of ARUPS to determine the symmetry and orientation of benzene on Pd(110). The benzene-derived photoemission bands show strongly anisotropic behavior in the two mirror planes of the (110) surface, and this is interpreted in terms of an inclination of the benzene molecular plane with respect to the surface plane. This tilting of benzene is a new observation; all previous reports of benzene adsorption indicate a parallel geometry.[4-12] The benzene molecules are arranged in a densely packed $c(4\times2)$ low-energy electron-diffraction (LEED) structure, azimuthally well ordered, and tilted towards the [001] direction, that is, into the grooves of the (110) surface, which decreases the intermolecular lateral repulsion.

The ARUPS experiments were carried out at the TGM 2 (toroidal grating monochromator) beam line of the synchrotron radiation laboratory BESSY in Berlin. Photoemission spectra were recorded in a modified VG ADES 400 angle-resolving spectrometer with a spherical sector analyzer, which can be rotated in two orthogonal planes. The total-energy resolution of the system (monochromator and analyzer) was set typically to 200 meV during the experiments reported here. Photoemission was measured with the photon polarization vector **E** parallel to the (001) and (1$\bar{1}$0) crystal mirror planes. (It is conventional to refer experimental azimuth planes to the direction along which they intersect the crystal surface: the Miller index of the [001] azimuth is (1$\bar{1}$0), and that of the [1$\bar{1}$0] azimuth is (001). The discussion here is exclusively in the azimuth notation.) s and p polarization were selected by changing the photon angle of incidence α from normal (s) to off normal (p). Photoelectrons were detected in both crystal azimuths as a function of the electron take-off angle θ. The Pd(110) surface was cleaned by Ar sputtering and annealing, and surface cleanliness and order were established by Auger spectroscopy, ultraviolet photoemission spectroscopy (UPS), and LEED. Benzene dosing was performed from the system ambient with the crystal at room temperature or at 80 K.

Exposing the clean (1×1) Pd(110) surface to ≈3 L of benzene [1 langmuir (L) $=10^{-6}$ Torr sec] at 300 K results in a very sharp $c(4\times2)$ LEED pattern. This pattern is unusually well developed for a molecule of the complexity of benzene. The work function decreases linearly to a saturation value of $\Delta\phi=-1.10$ eV (≈3 L exposure). Thermal desorption experiments reveal some molecular desorption (peak maximum at ≈410 K), but this is in competition with decomposition, as evidenced by H_2 release into the gas phase beyond 390 K. The benzene is, therefore, quite strongly bonded to the surface.

Figure 1 shows ARUPS spectra of benzene chemisorbed on Pd(110), excited by p polarized light, $h\nu=30.5$ eV. For comparison, a spectrum taken in normal emission ($\theta=0°$) from a condensed benzene layer is included in the figure, bottom curve. The molecular orbital (MO) content of the condensed benzene photoemission bands as derived from gas-phase photoemission and calculations[13,14]

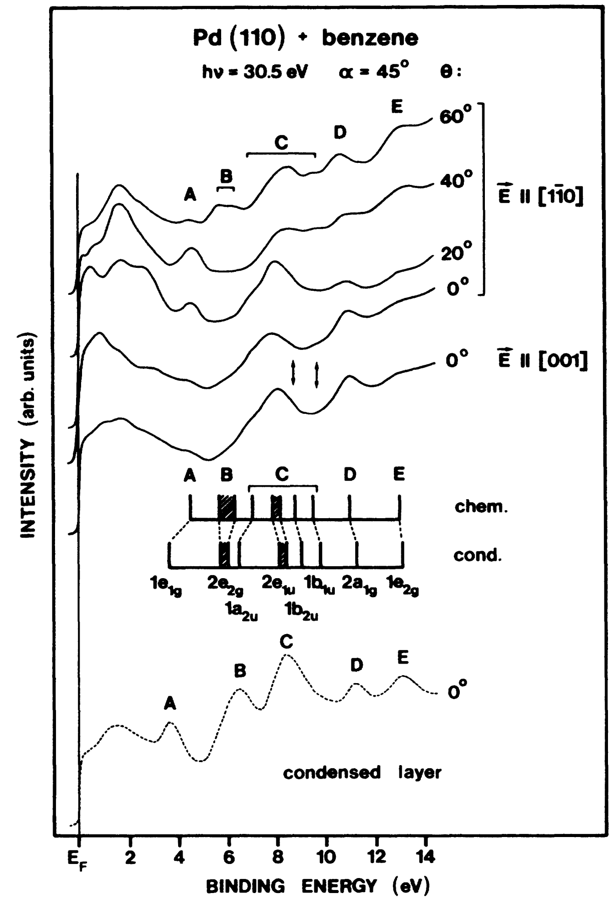

FIG. 1. Angle-resolved photoemission spectra of benzene on Pd(110). $h\nu = 30.5$ eV, *p* polarization, photon angle of incidence $\alpha = 45°$, electric vector lying within the azimuths indicated. For $\theta \neq 0°$ spectra were taken in the [1$\bar{1}$0] crystal azimuth.

is given in the form of a bar diagram. The association of the chemisorbed benzene bands *A*–*E* with MO's following well-established procedures[4-11] is shown in the upper bar diagram. This results in a relaxation shift of 0.25 eV to lower binding energy between the condensed and chemisorbed layer for the σ orbitals, but the π orbitals have to be treated in a different way.

Comparing the condensed benzene spectrum with normal emission spectra ($\theta = 0°$, Fig. 1) of the chemisorbed phase reveals significant differences. Band *A* ($1e_{1g},\pi$) decreases in intensity and shifts by 0.8 eV to *higher* binding energy, so relative to the σ bands these π bands shift down by about 1 eV. A similar stabilization is also seen for the $1a_{2u}$ π component of band *B*, which becomes the leading component of band *C* in the chemisorbed phase. These stabilizations, as in other benzene chemisorption systems,[4-11] signal a strong π bonding interaction with the metal surface. Bands *B* and *E* have little intensity in the $\theta = 0°$ spectra of chemisorbed benzene, but recover their intensity at higher emission angles. This is a symmetry-related effect and a result of selection rules.

The selection rules for normal emission separated into the various photon polarization components are contained in the correlation table (Table I), in which the MO's of benzene are transposed from D_{6h} to the lower C_{6v} and C_{2v} symmetries (columns 1–3). The C_{2v} symmetry considered in Table I has the C_2 axis perpendicular to the molecular plane to represent C_{2v} imposed on a flat lying benzene molecule. We notice that in C_{6v} symmetry, emission in the normal direction cannot be excited by any polarization component from the $2e_{2g}$, $1e_{2g}$, $1b_{2u}$, and $1b_{1u}$ orbitals; accordingly, bands $B(2e_{2g})$, $E(1e_{2g})$, and the higher-energy components of band *C* should be forbidden in normal emission spectra. Figure 1 reveals that at $\theta = 0°$ the intensity of these bands is indeed very weak. To a first approximation, C_{6v} symmetry seems, therefore, indicated.

There is, however, some intensity left in these bands as compared to other benzene adsorption systems.[5,6,8,9] This indicates that there is a small perturbation present which lowers the C_{6v} symmetry. Closer inspection of the two normal emission spectra in Fig. 1 recorded with the E vector alternatively in the [001] and [1$\bar{1}$0] azimuths shows some intensity differences in the Pd valence bands (between 0 and 3 eV) and, more relevant to the present discussion, in the higher-energy region of band *C* between 8–10 eV. This is the region of the $1b_{2u}$ and $1b_{1u}$ orbitals.

TABLE I. Correlation table of the molecular orbitals of benzene. Polarization components for allowed normal emission are indicated. The symmetry of MO's with respect to the [001] and [1$\bar{1}$0] azimuth of the (110) surface for a benzene molecule as oriented in Fig. 3 are given in columns 5 and 6. Note that the C_2 axis for C_{2v} corresponds to C_6^3 for the higher symmetries.

D_{6h}	C_{6v}		C_{2v}		Expt.	[001]	[1$\bar{1}$0]
$1e_{1g}$	e_1	x,y	b_1+b_2	$x+y$	*A*	u^a+g^b	$g+u$
$2e_{2g}$	e_2	$\cdots$	a_1+a_2	z	*B*	$g+u$	$g+u$
$1a_{2u}$	a_1	z	a_1	z		g	g
$2e_{1u}$	e_1	x,y	b_1+b_2	$x+y$	*C*	$u+g$	$g+u$
$1b_{2u}$	b_2	$\cdots$	b_2	y		g	u
$1b_{1u}$	b_1	$\cdots$	b_1	x		u	g
$2a_{1g}$	a_1	z	a_1	z	*D*	g	g
$1e_{2g}$	e_2	$\cdots$	a_1+a_2	z	*E*	$g+u$	$g+u$

[a] *u* designates odd symmetry with respect to mirror plane.

[b] *g* designates even symmetry with respect to mirror plane.

Dependence of normal emission on the photon azimuthal angle of incidence is possible for C_{2v} symmetry, since the orbitals with irreducible representations of b character are inequivalent in the x and y directions.[15] Note that for E parallel to the [001] azimuth the $1b_{2u}$ component (b_2 in C_{2v}, Table I) of band C is emphasized, whereas for E parallel to [1$\bar{1}$0] the $1b_{1u}$ MO (b_1 in C_{2v}) appears to be more prominent (see arrows in Fig. 1). This behavior suggests, therefore, a weak C_{2v} perturbation operating on the ring thus giving an indication that the [001] and [1$\bar{1}$0] directions are inequivalent for the molecular complex. This is substantiated by the different θ dependence of the spectra in the two crystal azimuths, and by the different dispersion of band D (Ref. 16).

Figure 2 shows photoemission spectra excited by s-polarized light with $h\nu = 46$ and 30.5 eV, recorded in the [001] and [1$\bar{1}$0] azimuths at $\theta = 55°$. In each case, spectra were measured with E parallel and perpendicular to these azimuths. If E is parallel to a mirror plane, emission into that mirror plane is only allowed from MO's with even symmetry, and this will be termed the "even geometry;" conversely, if E is perpendicular to that mirror plane, only MO's with odd symmetry can be observed ("odd geometry").[17] It is immediately apparent from Fig. 2 that strong effects between even (solid curves) and odd geometries (dashed curves) are observed in the [001] azimuth, but that the effects are very weak in the [1$\bar{1}$0] azimuth. In particular, in [001] the leading components of band C and band D have strong intensities in the even geometry, but are weak in the odd geometry. The $1b_{1u}$ component of band C, on the other hand, is stronger in the odd geometry, but the $1b_{2u}$ component appears to be more intense again in the even geometry. This is seen best at $h\nu = 30.5$ eV, and is emphasized in the figure by the box. For $h\nu = 46$ eV both b bands are too weak to demonstrate clearly any differences.

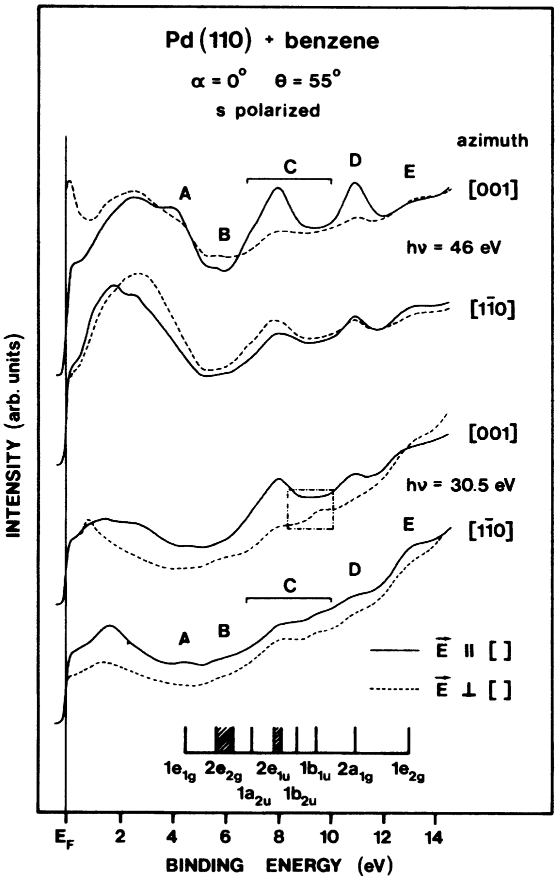

FIG. 2. Photoemission spectra of benzene on Pd(110) recorded at $\theta = 55°$ in the [001] and [1$\bar{1}$0] crystal azimuths with s polarized light. The photon polarization vector was either parallel (solid curves) or perpendicular (dashed curves) to the corresponding azimuths.

The results of the mirror plane emission experiments displayed in Fig. 2 indicate *azimuthal orientation* of the benzene molecules at the surface. Investigation of the symmetry of the benzene MO's with respect to the surface mirror planes can then yield the detailed orientation. In Table I, columns 5 and 6, the symmetry of the MO's with respect to the [001] and [1$\bar{1}$0] azimuthal plane is given for the azimuthal orientation shown in Fig. 3. Accordingly, the [001] and [1$\bar{1}$0] azimuths should be strictly equivalent on symmetry grounds for mirror plane emission in the even and odd geometry for the $1a_{2u}$ and the $2a_{1g}$ orbitals: both orbitals should have high intensity in the even and low intensity in the odd geometry in both azimuths. The absence of pronounced differences between even and odd geometry in the [1$\bar{1}$0] azimuth must therefore indicate that this is not a "good" mirror plane for the adsorption complex. This may be rationalized if the benzene mole-

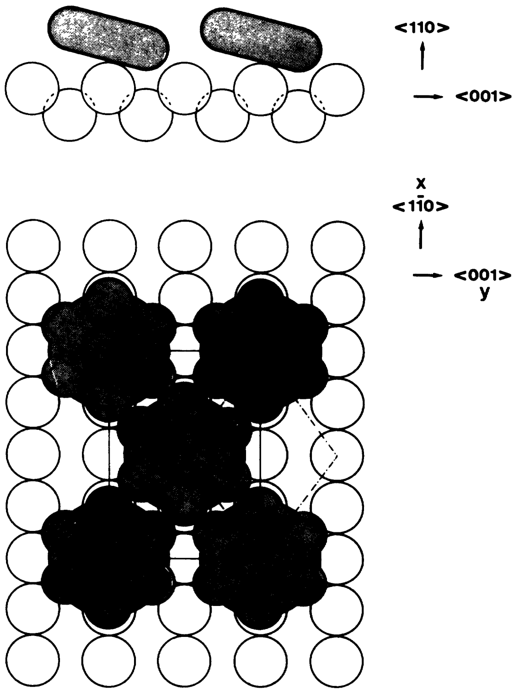

FIG. 3. Model of the $c(4\times2)$ structure of benzene on Pd(110) (top and side views). Both primitive (dashed) and centered (solid) unit cells are indicated. The benzene molecules are represented by their respective van der Waals radii.

cules are tilted towards the [001] direction, thus obliterating the mirror character of the $[1\bar{1}0]$ azimuth plane for the adsorption complex while retaining that of the [001] azimuth plane. The symmetry is then actually lower than C_{2v}, viz., $C_{s,\sigma v}$ with σ_v coinciding with the [001] azimuth. The behavior of the *b* orbitals allows us to determine the exact orientation. For the orientation considered in Fig. 3, the b_{2u}-derived orbital should be even, and the b_{1u} orbital odd in the [001] azimuth, and this is, in fact, observed in Fig. 2.

A model of the structure of benzene on Pd(110) is displayed in Fig. 3. Both primitive and centered unit cells of the $c(4\times 2)$ structure are indicated, and the orientation of the benzene molecules is shown as derived above. The size of the molecules is represented by the van der Waals radii of H and C atoms resulting in a rather densely packed adlayer structure. We note that the arrangement shown in Fig. 3 is the only one possible for the given LEED structure without extensive overlapping of H atoms within their van der Waals radii. Thus, ARUPS analysis and LEED evidence are in excellent agreement. The tilt determined from ARUPS has a ready interpretation in terms of the structure shown, in that a tilt towards the [001] direction, that is, into the grooves of the (110) surface as sketched by the side view in Fig. 3, further reduces intermolecular repulsions. As to the inclination angle, an educated guess considering the θ dependence of benzene bands in the [001] and $[1\bar{1}0]$ azimuth suggests a value between 10° and 20°. The different dispersions of band *D* along $[1\bar{1}0]$ and [001],[16] amounting to maximum values of 400 and 200 meV, respectively, point out stronger intermolecular interactions in $[1\bar{1}0]$ than in [001]. This is consistent with the inclination as modeled in Fig. 3. Theoretical calculations of the dispersion for different intermolecular H atoms distances should allow us to specify the tilting angle more accurately, and such calculations are presently underway.[16]

In summary, the gross features of ARUPS behavior of benzene on Pd(110) suggest C_{6v} symmetry of the adsorption complex, but more detailed analysis reveals a symmetry distortion towards $C_{s,\sigma v}$. The C_{6v} symmetry may be representative of the *intramolecular* geometry, but the C_s symmetry reflects the orientation with respect to the *underlying substrate*. Photoemission with polarized synchrotron radiation in the two mirror planes of the (110) surface in conjunction with a well-ordered LEED pattern allows us to specify the adsorbate structure in a rather detailed way: the benzene molecules are azimuthally oriented, corners along $[1\bar{1}0]$, and tilted into the [001] direction with an inclination angle of the order 10–20°.

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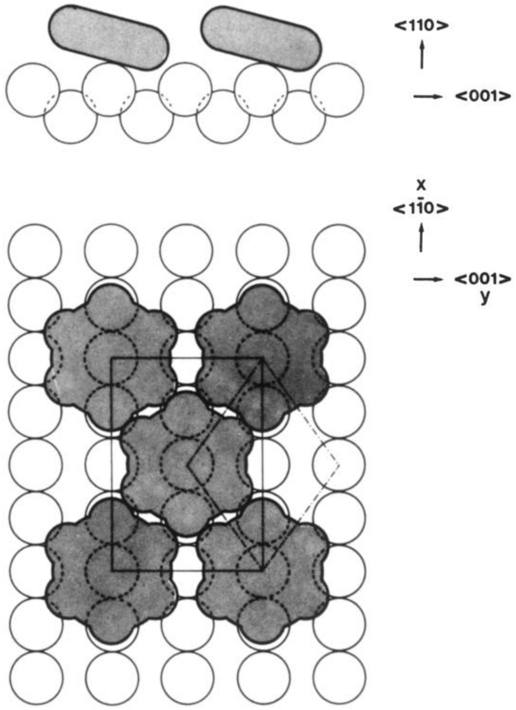

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