NEXAFS Study on the Orientation of Chiral P-Heptahelicene on Ni(100)

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Received September 5, 2000

Abstract: Near-edge X-ray absorption spectroscopy with linearly polarized synchrotron radiation has been applied to study the orientation of the helically shaped polyaromatic hydrocarbon P-heptahelicene ($C_{30}H_{12}$) on a Ni(100) surface under ultrahigh vacuum (UHV) conditions. By measuring the polarization dependence of the C1s → π^* transitions the local adsorption geometry was determined. Between the helical axis of the molecule and the surface plane an angle of 43 ± 5° was observed for a saturated monolayer.

1. Introduction

Chiral surfaces are of interest in research areas such as stereoselective chemical synthesis, separation of chiral compounds, crystal growth, and adsorption of proteins.[1] In particular, chiral surfaces are predicted to have outstanding nonlinear optical activity.[2−6] To generate a well-defined model system for optical studies on chiral surfaces, we prepared a closed-packed monolayer of chiral molecules. For this purpose, we adsorbed heptahelicene (Figure 1) on metal single-crystal surfaces under UHV conditions.[7−9] The aromatic π-electron system of this phenanthrene derivative is delocalized over the helical backbone resulting in a pronounced optical activity.[10] Heptahelicene ([7]H) was synthesized for the first time in 1967 from stilbene derivatives via photocyclodehydrogenation.[11] Its enthalpy for thermal racemization of 167 kJ/mol in solution is sufficiently high for sublimation in UHV.[10]

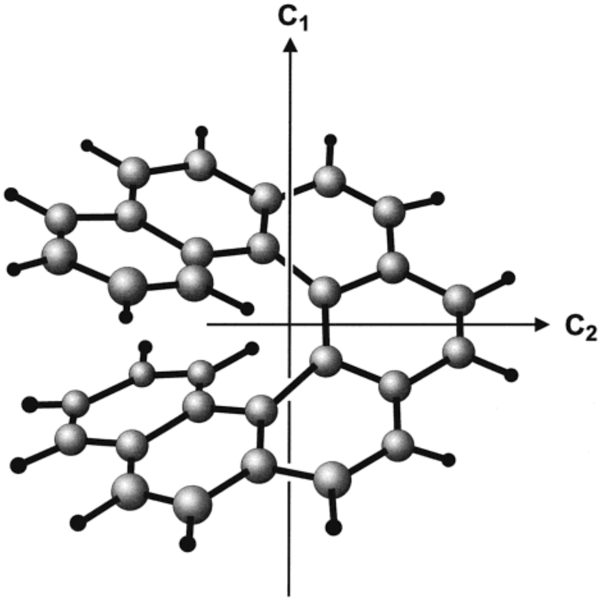

Figure 1. Structure and symmetry axes of P-[7]helicene, $C_{30}H_{18}$.

Studies of planar aromatic hydrocarbons (e.g., benzene, naphthalene, coronene, and perylene) on metal single-crystal surfaces and on highly oriented pyrolytic graphite showed that these molecules are usually adsorbed in a geometry with the ring plane oriented parallel to the surface plane.[12] However, there are examples for aromatic hydrocarbons where the molecular plane is perpendicular or tilted with respect to the surface, e.g., tetracene on Cu(100) was found to be adsorbed with the ring plane parallel to the surface normal.[13]

The aim of our studies was to determine the orientation of [7]H in the closed-packed saturated monolayer structure on Ni(100). Angle dependent Near Edge X-ray Absorption Fine Structure (NEXAFS) measurement with polarized synchrotron radiation is a suitable method to determine the adsorption

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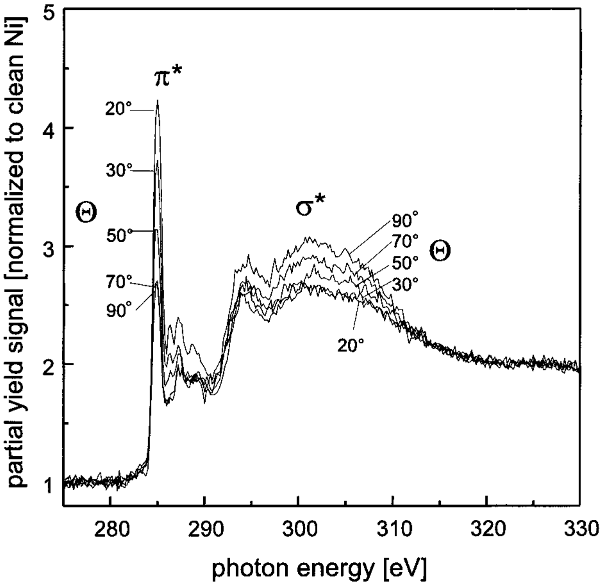

Figure 2. Polar angle series of C1s-NEXAFS spectra taken from the saturated monolayer of P-[7]helicene on Ni(100).

geometry of planar aromatic molecules.[14] Here we show that NEXAFS can be applied also to determine the adsorption geometry of a helical molecule.

2. Experimental Section

Racemic mixtures of [7]H were synthesized as described previously.[15] The separation and assignment of the enantiomers was performed via high-performance liquid chromatography (HPLC) and via CD spectroscopy in combination with data known from the literature.[10] The experiments were carried out at the Berlin storage ring for synchrotron radiation (BESSY) using the SX-700-III monochromator. NEXAFS spectra were recorded at the carbon K edge region ($h\nu = 275-330$ eV) in partial yield mode and were normalized to the clean substrate. The sample was irradiated with linearly parallel polarized light (p-pol) at different polar angles (±2°) from normal incidence ($\Theta = 90°$) to grazing incidence ($\Theta = 20°$), resulting in geometries with the electric field vector parallel to the surface or almost perpendicular to the surface, respectively. The nickel substrate was sputter cleaned and annealed. P-[7]H was adsorbed in vacuo by exposure of the Ni(100) surface to a molecular beam generated in a Knudsen cell at 440 K. After deposition of multilayered films the monolayer was prepared by momentarily heating the sample to 380 K. This induced a desorption of [7]H, as observed with a mass spectrometer located above the Ni(100) sample. The aforementioned studies on the interaction of [7]H with the Ni(111) surface[7] and the Cu(111) surface[9] showed that this procedure caused the desorption of [7]H from the multilayers and the second layer only, leaving a monolayer of [7]H on the surface. Heating the monolayer to higher temperatures caused decomposition into carbon and hydrogen. The latter desorbs as H_2, again detected via thermal desorption mass spectrometry (TDMS). This decomposition step was confirmed here for Ni(100) via TDMS as well, indicating also the formation of the saturated [7]H monolayer on the surface. During exposure and measurement the sample was at room temperature. After the NEXAFS studies, the optical purity of [7]H in the Knudsen cell, as well as the recondensed [7]H on the shutter of the cell, was checked via HPLC. Only the P-enantiomer was detected, indicating that no racemization occurred.

3. Results and Discussion

Figure 2 shows NEXAFS spectra as a function of the polar angle. Two kinds of resonances are observed in the near-carbon K-edge spectral range: π^*-resonances (285 and 288 eV) and σ^*-resonances (292 to 315 eV). With increasing polar angles the intensities of the π^*-resonances at 285 and 288 eV decrease. Hence, the highest π^*-resonance intensity results for grazing incidence, the lowest for normal incidence. The opposite trend is observed in the case of the σ^*-resonances. The spectra for angles of 90° and 70° show no difference in the π^*-resonance intensity, while the σ^*-resonance intensities at angles of 20° and 30° are identical.

The resonance intensity dependence can be described by reference to the dipole selection rules governing the excitation from the C1s level into the unoccupied orbitals π^* and σ^*. The excitations into π^* and σ^* final states depend on the molecular orientation with respect to the electric field vector of the polarized light. With the molecules aligned on the surface, the resonance intensity as a function of the sample orientation provides information on the orientation of the molecules on the surface.[16] For a planar aromatic molecule (e.g. benzene), the C1s → π^* transition is polarized perpendicular to the molecular plane.[17] Thus, within the dipole approximation this transition is forbidden when the electric field vector is oriented parallel to the molecular plane, and has maximum intensity when the electric field vector is oriented perpendicular to the molecular plane. Hence, if the benzene molecule is adsorbed with its molecular plane parallel to the surface, the C1s → π^* transition has minimal intensity at normal incidence and maximum intensity at grazing incidence. Vice versa, the C1s → σ^* transition intensity is at maximum at normal incidence, because it is polarized parallel to the molecular plane. However, this particular dependence on the angle of incidence is only valid for p-polarized light, i.e., when the electric field vector is parallel to the plane of incidence. The intensity variation of the C1s → π^* excitation, as a function of the angle between the molecular plane and the surface (α), is given by:[13,14]

$$I_\pi(\Theta,\alpha) \sim P(\sin^2\alpha\,\sin^2\Theta + 2\cos^2\alpha\,\cos^2\Theta) + (1-P)\sin^2\alpha \quad (1)$$

Θ is the angle of incidence and P the degree of linear polarization of the synchrotron radiation. This equation holds only for surfaces with 3-fold symmetry or higher, i.e., the effect of azimuthal orientation of the tilted molecules in different domains cancels.[14] The observation that at normal incidence the C1s → π^* resonance intensity is at minimum allows the conclusion that on average the angle of the ring planes of [7]H is tilted less than 55° with respect to the surface plane. The simulation of the intensity dependence for different tilt angles α ($P = 0.87$[18]) compared to our data is shown in Figure 3. The best fit yields an apparent tilt angle of 43 ± 5°.

For [7]H it is reasonable to assume that the C1s → π^* transitions are still polarized perpendicular to the ring planes. However, because [7]H is not planar, we must consider the intramolecular tilt of the C1s → π^* polarization vectors with respect to the molecular axes, e.g., the C_1-axis and C_2-axis. From X-ray crystallography studies on [7]H an angle of 15° between each ring normal, i.e., the polarization vector of the C1s → π^* transition, and the C_1-axis can be deduced.[19] Hence, when the electric field vector of the X-ray radiation is oriented perpen-

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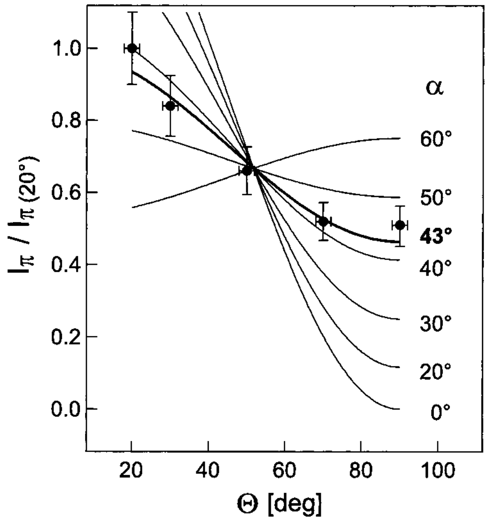

Figure 3. C1s → π* resonance intensities normalized to the intensity at grazing incidence (20°). The best fit for the intensity dependence of the angle of light incidence is found for an apparent tilt angle of 43° (thick line). From the degree of polarization of the synchrotron radiation an error of 10% was estimated for the intensity ratios.

dicular to the molecular C_1-axis (i.e. the helical axis), minimum intensity for the π*-transition should be expected; and maximum intensity should be observed when the electric field vector is oriented parallel to the C_1-axis. Assuming that the molecular structure is not changed due to adsorption and by addition of the transition vectors of all seven rings, one can predict the results for particular adsorption geometries. For instance, if the molecule is adsorbed with the C_1-axis perpendicular to the surface and a random rotation around C_1 is allowed, an apparent tilt angle of 15° should be observed. For the same reason, tilt angles lower than 15° are not observable. In case of an adsorption geometry with the C_2-axis perpendicular to the surface, i.e., the helical axis lies parallel to the surface plane, an angle of 90° must be obtained. In this case, the contributions from the rings 1−3 cancel with those from the rings 5−7 because of the local C_2 symmetry.

The helical molecular structure is finally brought into accord with the best-fit result of 43 ± 5°, when the angle between the surface plane and the C_1-axis is considered to be about this value. For this geometry, however, no further conclusions on the orientation of the C_2-axis can be drawn. The variation in the average tilt value under rotation around C_1 amounts here to only a few degrees.[20] A parallel orientation of the C_2-axes of all molecules in a C_1-tilted geometry would actually not lead to the highest density in the monolayer. A denser stacking is realized when adjacent helicene molecules are rotated around C_1 with respect to each other.

Depending on the adsorption energy or the reactivity on the surface, the molecular orientation of aromatic molecules can indeed vary with coverage or temperature, respectively.[21] Since no decomposition of [7]H, i.e., hydrogen desorption, was observed below 550 K, one can exclude that the tilt is induced by a chemical reaction with the substrate upon annealing to 380 K during preparation. For the saturated monolayer of benzene on Cu(111) a tilt angle of about 20° was deduced while the molecule is adsorbed parallel to the surface at lower coverages.[22] At low coverage, aromatic hydrocarbons adsorbed at room temperature on nickel surfaces are bound to the substrate through the π-orbitals.[23−25] Hence, one may expect that [7]H is initially adsorbed with one or two aromatic rings oriented parallel to the surface, leading to a geometry where the molecule spirals away from the surface. However, only a small tilt angle of the helical axis of about 15° should be observed for that adsorption geometry. For isolated [7]H molecules on Ni(111), our STM studies indicate such a geometry,[7] and at low coverages on Cu(111) this geometry was confirmed via photoelectron diffraction.[9] However, no reliable information on the local geometry in the closed-packed layers has been obtained from these studies; the molecules could be tilted at saturation as well. The monolayer coverage at saturation of [7]H on Cu(111) was determined as 0.048. Every molecule covers an area equivalent to 21 substrate atoms, i.e., 133 Å^2.[8] The unit cell for [7]H on Ni(111) was found to be as big as 16 to 25 Ni atoms[7] and it is reasonable to assume a similar monolayer density for the [7]H/Ni(100) system. However, the average value of 21 Ni(111) surface atoms already should be the lower limit for a "parallel" geometry. The resulting area of 113 Å^2, which is equivalent to 18 Ni(100) surface atoms, is completely covered by a [7]H molecule, if its van der Waals radius of 6 Å perpendicular to the C_1-axis is considered. At this minimum distance, the lateral interactions become more dominant. In particular, the intermolecular π−π-interactions in closed-packed layers build up from bigger aromatic molecules favors nonaxisparallel adsorption geometries.[12]

Acknowledgment. Financial support by the Schweizer Nationalfonds (NFP 36) and the BMBF Germany is gratefully acknowledged.

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[20] Because of an additional interplanar angle between the terminal rings of 30° (ref 19), rotation around C_1 has an influence. However, the average angles between the ring planes and the surface plane for C_1 and C_2 at 45° or C_1 at 45° and C_2 at 0° are calculated as 41° and 45°, respectively.

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