

Orientation of chiral heptahelicene $C_{30}H_{18}$ on copper surfaces: An x-ray photoelectron diffraction study

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The orientation and the intramolecular relaxation due to adsorption of the chiral phenanthrene-derivative heptahelicene, $C_{30}H_{18}$, on Cu(111) and Cu(332) surfaces have been investigated by means of angle-scanned full-hemispherical x-ray photoelectron diffraction. Although the C 1s diffraction patterns of the adsorbed submonolayer coverage helicene films exhibit scattering anisotropies of less than two percent, a detailed analysis involving simple molecular mechanics calculations of the atomic coordinates, photoelectron diffraction single-scattering cluster calculations and an *R*-factor analysis permits the determination of the helicene molecular orientation. On Cu(111), the molecules are found to bind to the substrate surface via their terminal phenanthrene group oriented parallel to the surface plane, while on Cu(332) the three terminal C-6 rings are oriented parallel to the (111) terrace plane. Six azimuthal molecular orientations are found to coexist on Cu(111), on Cu(332), however, the step–molecule interaction leads to a unique azimuthal alignment of the heptahelicene molecules. The heptahelicene on Cu(332) system thus represents a chiral surface with single-phase orientational order. © 2001 American Institute of Physics. [DOI: 10.1063/1.1377886]

INTRODUCTION

Since the pioneering work of Pasteur,¹ the presence of chirality in nature and stereospecificity in chemical reactions has intrigued generations of researchers. Chiral surfaces have been of interest in applications such as stereoselective chemical synthesis and catalysis, separation of chiral compounds, crystal growth, protein adsorption and optical activity.² Recently, the adsorption and assembly of chiral molecules on solid surfaces has become a particularly fascinating area of study. Organized organic films of chiral molecules have been reported to asymmetrically scatter polarized electrons, suggesting their application as a source of highly polarized electron beams.³ Their high scattering asymmetry was explained in terms of coherent interaction of the long-wavelength electrons with many chiral centers. A strong enhancement of nonlinear optical properties through supramolecular chirality has been reported, with suggestions to use helicenes in a quasi-phase-matched structure to achieve phase matching in frequency conversion.⁴ Very recently, the role of extended surface chirality from supramolecular assemblies of adsorbed chiral molecules in a heterogeneous enantioselective catalytic reaction was unraveled for the first time.⁵ Although very different with respect to the particular system and properties studied, these few examples consistently point out the importance of molecular order. With the aim of fabricating a chiral surface exhibiting maximum molecular order—single-

phase translational *and* orientational order—for nonlinear optical studies, we have studied the adsorption of heptahelicene on two copper single-crystal surfaces.

The helicenes, first synthesized in 1956 by Newmann,⁶ are a fascinating class of chiral molecules. Helicenes are benzologs of phenanthrene in which a regular cylindrical helix is formed through an all-ortho annelation of the aromatic rings. Their helical structure is a consequence of the repulsive steric interaction between terminal aromatic rings. Helicenes possess a number of unusual and interesting physical properties, as, for instance, large optical rotation. Recent calculations of the electronic conductance of helicenes⁷ even indicate that a helicene can be made semiconducting or metallic by tuning the radius of the helix and the width of the helix ribbon. This might allow the construction of a semiconductor–metal–semiconductor helicene hybrid which would be the molecular realization of a quantum dot.

We have been investigating monomolecular films of chiral heptahelicene adsorbed on single-crystalline surfaces by means of different experimental techniques,⁸ including temperature-programmed desorption, low-energy electron diffraction (LEED) and scanning tunneling microscopy. Heptahelicene (Fig. 1) is a polyaromatic phenanthrene derivative and has a π -electron system (30 electrons) delocalized over the helical backbone, resulting in pronounced optical activity. For example, a value of 5900° was measured for the molecular optical rotation of the *M*-enantiomer in solution.⁹ Because of the high polarizability and hyperpolarizability of the π -electrons, a significant second-order electro-optic response of heptahelicene is predicted.¹⁰ Here,

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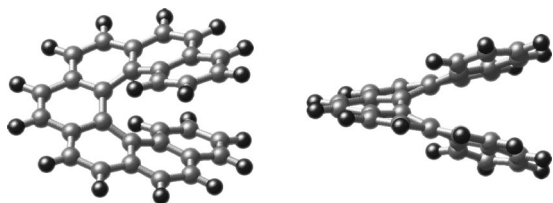


FIG. 1. Structure of the *M*-enantiomer of heptahelicene: perspective views.

we report on the adsorption of heptahelicene $C_{30}H_{18}$ (Fig. 1) on two copper surfaces, namely the Cu(111) surface and the related, stepped Cu(332) surface which consists of 12 Å wide (111) terraces separated by monoatomic steps. We focus on two key properties of molecular films: the molecular orientation and the intramolecular rearrangement upon adsorption.

For molecules larger than a few atoms, the determination of molecular orientation is by no means a trivial task. Most of the traditional structural methods fail in the case of too many atoms per unit cell, and spectroscopic methods probing transition matrix elements rely on the existence of a few but well defined and separated symmetry elements. As recently shown for the case of fullerene C_{60} molecules on different single-crystalline surfaces, angle-scanned x-ray photoelectron diffraction (XPD)¹¹ permits a rather direct and unambiguous determination of the orientation of “large” adsorbed molecules. We have therefore applied this method to heptahelicene $C_{30}H_{18}$ on Cu(111) and Cu(332), investigating the orientation of helicene molecules in monomolecular films.

EXPERIMENT

The heptahelicene molecules were synthesized as described elsewhere.¹² The two enantiomers, called *M*-heptahelicene (Minus) and *P*-heptahelicene (Plus), were separated using high-performance liquid chromatography techniques.¹³ For the experiments reported here, only the “left-handed” *M*-heptahelicene as shown in Fig. 1 was used.

The copper single-crystal substrate surfaces were prepared by standard Ar^+ -sputtering and annealing cycles. Before deposition of heptahelicene molecules, cleanliness and surface order were monitored by core-level photoemission (XPS) and LEED, respectively. Submonolayer quantities of heptahelicene were deposited onto the copper surfaces by sublimation from a Knudsen type evaporator at 440 K. In order to avoid multilayer coverages and to maximize the mobility of the molecules during adsorption, the substrate was kept at a temperature of 440 K—roughly half way in between the maximum of the multilayer thermal desorption spectrum at 370 K and the maximum of the monolayer thermal desorption spectrum at 530 K⁸—during deposition.

The coverage of the heptahelicene films was determined from the C 1s to Cu 3s photoelectron intensity ratio. A calibration of this ratio was performed by deposition of a few monolayers of C_{60} onto the Cu(111) surface and subsequent annealing above the C_{60} sublimation temperature of 575 K. This procedure is well known¹⁴ to result in a close-packed monolayer of C_{60} with a (4×4) -superstructure where one C_{60} molecule corresponds to 16 copper surface atoms, or—in

other words—60 C-atoms per 16 Cu-surface unit cells. From this calibration, we find that the heptahelicene films obtained as described above consist of one molecule per every 61 Cu surface unit cells. As the close-packed monolayer of heptahelicene on Cu(111) displays a LEED pattern with a $\begin{pmatrix} 5 & 1 \\ -1 & 4 \end{pmatrix}$ unit cell, corresponding to one molecule per every 21 Cu-atoms,⁸ it follows that the coverage of the films prepared as described above is 1/3 of a close-packed monolayer.

The XPD experiments were performed in the University of Zurich’s VG ESCALAB 220 spectrometer equipped for motorized sequential angle-scanning data acquisition.¹⁵ C 1s photoelectron diffraction patterns from the heptahelicene films were acquired using nonmonochromatized $MgK\alpha$ excitation ($h\nu = 1253.6$ eV). In order to minimize the effect of thermal vibrations of the adsorbed molecules on the scattering anisotropies, the sample was kept at 150 K during data acquisition. Care was taken to ensure that prolonged exposure to the x-ray beam did not deteriorate the molecular films. It was verified that—apart from counting statistics—acquisition times between 90 and 900 minutes gave identical diffraction patterns. Coverage and cleanliness of the films were monitored before and after each acquisition of a diffraction pattern.

HEPTAHELICENE ON Cu(111): EXPERIMENTAL RESULTS

The experimental C 1s XPD pattern from a 1/3 ML coverage film of *M*-heptahelicene on Cu(111) is shown in Fig. 2(a). In order to increase the statistical accuracy, the pattern has been threefold rotationally averaged according to the symmetry of the Cu(111) substrate surface. It has been verified that this procedure does not introduce features that are absent in the raw data. The resulting pattern exhibited an intrinsic sixfold rotational symmetry, and we therefore applied a further twofold rotational averaging to the data. The smooth polar-angle dependent background typical for adsorbate emission has been removed by dividing the intensity of each data point by the intensity at the corresponding polar angle averaged over all azimuthal angles. The diffraction intensities are shown in stereographic projection and in a linear gray scale with maximum intensity corresponding to white. The orientation of the substrate as determined from a Cu LMM Auger-electron diffraction pattern from the clean Cu(111) surface [Fig. 2(b)] is indicated.

The heptahelicene C 1s diffraction pattern exhibits a sixfold rotational symmetry, with the strongest anisotropy appearing in a wheel-type feature close to the center of the plot. Given the fact that the free heptahelicene molecule only possesses a twofold rotational (C_2) symmetry axis, this observation immediately tells that the molecules exist in at least three distinct orientations on the surface. As the fcc Cu(111) surface itself has sixfold or threefold symmetry—depending on whether only the first or also the second layer are considered—the occurrence of at least three domains is expected. On the other hand, the observation of diffraction anisotropy immediately indicates orientational order, i.e., the adsorbed molecules take distinct orientational configurations. Taking into account that increased diffraction intensity in an XPD experiment is mainly observed along directions of

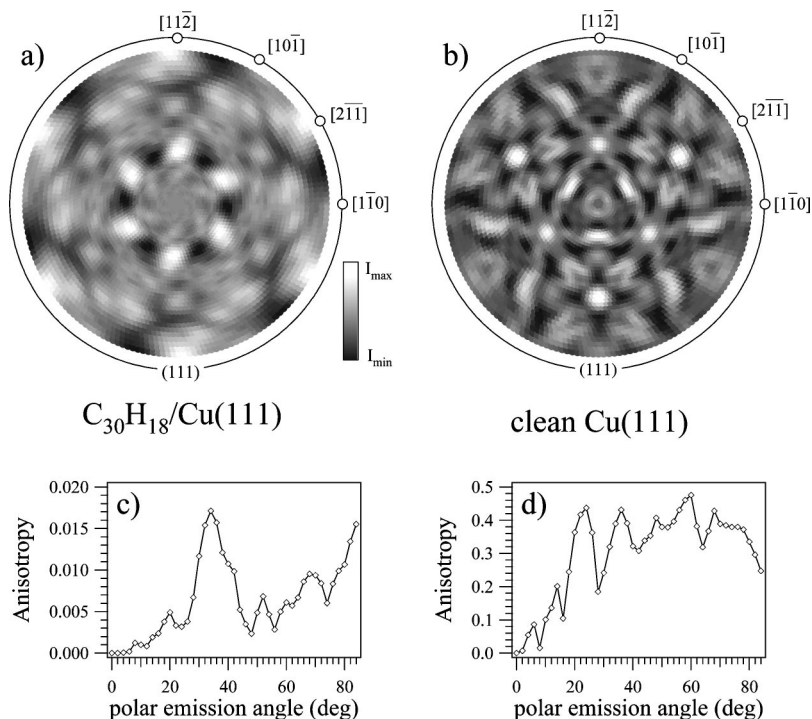


FIG. 2. (a) Angle-scanned x-ray photoelectron diffraction pattern for C 1s emission from the *M*-enantiomer of heptahelicene on Cu(111). (b) Cu LMM Auger-electron diffraction pattern from the clean Cu(111) surface. (c) and (d) Diffraction anisotropy (see the text) as a function of the polar emission angle determined from the patterns in (a) and (b), respectively.

near-neighbor emitter–scatterer pairs,^{11,16} randomly oriented emitter–scatterer pairs, as would be the case for orientationally disordered molecules, would not give an overall intensity enhancement along any direction. We thus conclude that (at least the majority of) the heptahelicene molecules exist in well-defined orientational configurations.

Before moving on to a discussion of the calculations that we have performed in order to determine what orientations of the molecules are responsible for the observed diffraction pattern, we would like to mention the low anisotropy of this pattern. Figure 2(c) shows a plot of the helicene C 1s azimuthal diffraction anisotropy $A = (I_{max} - I_{min})/I_{max}$, where I_{max} and I_{min} are the maximum and minimum intensities observed at a particular polar emission angle, as a function of polar emission angle. For comparison, the same quantity is shown in Fig. 2(d) for the Cu(111) substrate diffraction pattern [Fig. 2(b)]. Whereas the anisotropies in the substrate pattern are in the 40–50% range, the helicene C 1s pattern exhibits anisotropies lower than 2%. This extremely low anisotropy puts the most stringent requirements on the background subtraction procedure involved in the determination of the C 1s photoelectron intensities: in order not to be spuriously affected by diffraction features inherently present in the inelastic photoelectron background,¹⁷ a most reliable procedure for the determination of the low-anisotropy helicene C 1s diffraction intensities has to be employed. We were very attentive to this point and performed an accurate calibration of the relative efficiencies of the six channeltrons of the electron energy analyzer. The C 1s diffraction intensity was determined by a linear subtraction procedure using the channeltron-efficiency-corrected count rates of the channeltron located at the C 1s peak energy and the two channeltrons at the high and low energy footpoints of the peak. Although rather simple, this procedure proved to be very effective in separating C 1s and background intensity dif-

fraction features. Note that the pattern shown in Fig. 2(a) has been obtained by summing the results of three different (but identical) measurements, two long acquisitions of 13 hours and one shorter acquisition of 2 hours, and thus represents a total acquisition time of 21.5 seconds at each of the 4686 different angular settings. These long counting times were needed in order to accurately extract the aforementioned low-anisotropy diffraction intensities.

Qualitatively, low diffraction anisotropies are in fact expected for C 1s emission from a molecule with low symmetry like heptahelicene. Each of the 30 C-atoms of each heptahelicene molecule acts as a photoemitter and the resulting photoelectron waves are scattered from all the other 29 C-atoms,¹⁸ which leads to a total of 30×29 inequivalent emitter–scatterer directions. Unlike in the case of a highly symmetric molecule like C_{60} , where many different C–C emitter–scatterer pairs contribute to an add-up of intensity along a common direction and anisotropies can reach up to 20%, for heptahelicene the intensity enhancements due to the forward-focusing effect are distributed rather uniformly among all emission angles. Consequently, a lower total scattering anisotropy is expected. Furthermore, thermally induced vibrations of the C-atoms or librations of the entire molecular skeleton are expected to be significant for a “floppy” molecule like helicene, which results in a smearing-out of diffraction features and, therefore, to a further lowering of the observed anisotropy.

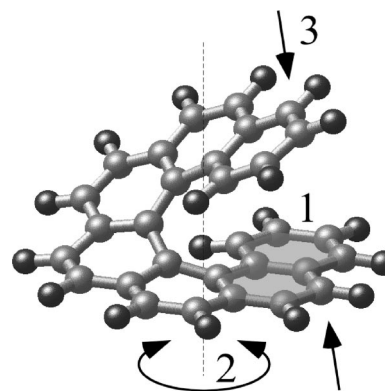
HEPTAHELICENE ON Cu(111): SCATTERING CALCULATIONS AND DISCUSSION

In order to determine what orientation(s) of the heptahelicene molecules give(s) rise to the experimental C 1s diffraction pattern shown in Fig. 2(a), we performed scattering calculations for a variety of molecular conformations and

orientations with respect to the substrate surface. All calculations were done using a modified single-scattering cluster (SSC) calculation scheme as implemented by Friedman and Fadley,¹⁹ including spherical wave corrections.²⁰ We have previously shown that, using this approach, the diffraction patterns from C_{60} molecules adsorbed on various surfaces can be accurately reproduced and the corresponding molecular orientation thus determined in a rather straightforward way.¹⁶ Briefly, given an assumed molecular conformation and orientation with respect to the surface, the SSC code simulates the corresponding XPD pattern by calculating for every photoelectron emitter and for every emission angle the amplitudes of the directly emitted photoelectron waves and of the waves scattered from all the other atoms. The interference between directly emitted and scattered waves is properly taken into account. The nonstructural input parameters are the inelastic mean free path of the emitted photoelectrons, the “effective” inner potential giving rise to refraction of the outgoing wave at the surface-to-vacuum boundary, and the atom’s mean square amplitudes of thermal vibration. For our analysis, the following values were used, given in the same sequence as above: 30 Å, 5 eV, 0.03 Å².²¹ The scattering phase shifts describing the C scattering strength for electrons of 970 eV kinetic energy were calculated using the MUFFOT code²² which is based on a muffin-tin approximation of the potential. The agreement between a SSC calculation and the experimental XPD pattern was quantified using the reliability-factor R_{MP} .²³

As a starting point in our analysis, the atomic coordinates of the *M*-enantiomer of heptahelicene as determined by x-ray diffraction from crystalline samples²⁴ were used. In other words, we assumed the molecule to retain its “shape” upon adsorption, and considered as an only degree of freedom the orientation of the molecule with respect to the substrate surface. This orientation can be handily described by a set of three Eulerian angles (α , β , γ), which we varied on a dense grid over the full 2π range in our SSC calculations. The resulting SSC calculations, however, did not even reproduce the most prominent features of the experimental diffraction pattern for any molecular orientation. We concluded, therefore, that the assumption of a rigid molecular skeleton was not adequate.

Given the large number of atomic coordinates to be determined, a structural analysis without any assumption about the molecular conformation is not feasible for computational reasons. We thus employed the following strategy to circumvent this limitation: first, a “reasonable” modification of a part of the molecular skeleton with respect to the one of the free molecule was chosen, i.e., some of the molecular coordinates were arbitrarily chosen (see below). With the conformation of that part of the molecule imposed, the remaining atomic coordinates were then optimized with respect to minimum total energy by means of simple molecular mechanics calculations, yielding the minimum energy geometry of the molecule under the ancillary condition of the arbitrary chosen and fixed molecular coordinates. These molecular mechanics geometry optimization calculations were done with the HyperChem calculation package²⁵ using the MM+ force field.²⁶ The resulting atomic coordinates of the heptahelicene



Structural parameters

FIG. 3. An illustration of the structural parameters considered in the analysis (see the text for more details).

molecule were finally used as input for the SSC calculations, the orientation of the molecule with respect to the surface varied on a dense grid of Eulerian angles, and the agreement between the resulting SSC calculation and the experimental pattern quantified by the R_{MP} -factor. Using this procedure of choosing and fixing the coordinates of one part of the molecule and optimizing the remaining coordinates we aimed at determining the intramolecular relaxation due to adsorption which otherwise, as mentioned above, is not computationally feasible.

Among the many modifications of the molecular skeleton that we considered, only the assumption of planar terminal C-6 rings oriented parallel to the substrate surface produced a minimum energy molecular conformation resulting in SSC calculations that came close to reproducing the experimental $C1s$ diffraction pattern of Fig. 2(a). Therefore, the idea of planar terminal C-6 rings bonding to the substrate surface was followed in detail. The structural parameters that were taken as degrees of freedom in the analysis are illustrated in Fig. 3: (1) Molecular mechanics geometry optimization calculations were done for heptahelicene molecules with 1, 2, 3, and 4 terminal C-6 rings confined in a planar configuration. (2) The resulting minimum energy coordinates were then used as input to the SSC calculations where the azimuthal orientation of the molecule was allowed to take any value between 0 and 360 degrees. Furthermore, the coexistence of three rotational domains (azimuthal orientations of the molecule) due to the symmetry of the Cu(111) surface was allowed. (3) In order to take into account possible deviations of the molecular pitch from the one obtained from the molecular mechanics calculations, a “pitch renormalization factor” was introduced into the SSC calculations by linearly scaling the atomic coordinates along the direction perpendicular to the surface.²⁷ This pitch renormalization is motivated by the assumption that the heptahelicene molecule might differently spiral away from its terminal planar ring(s) due to the interaction with the underlying Cu(111) surface than without any substrate interaction—which is the case considered in the molecular mechanics model. In other words, the renormalization factor was introduced in order to

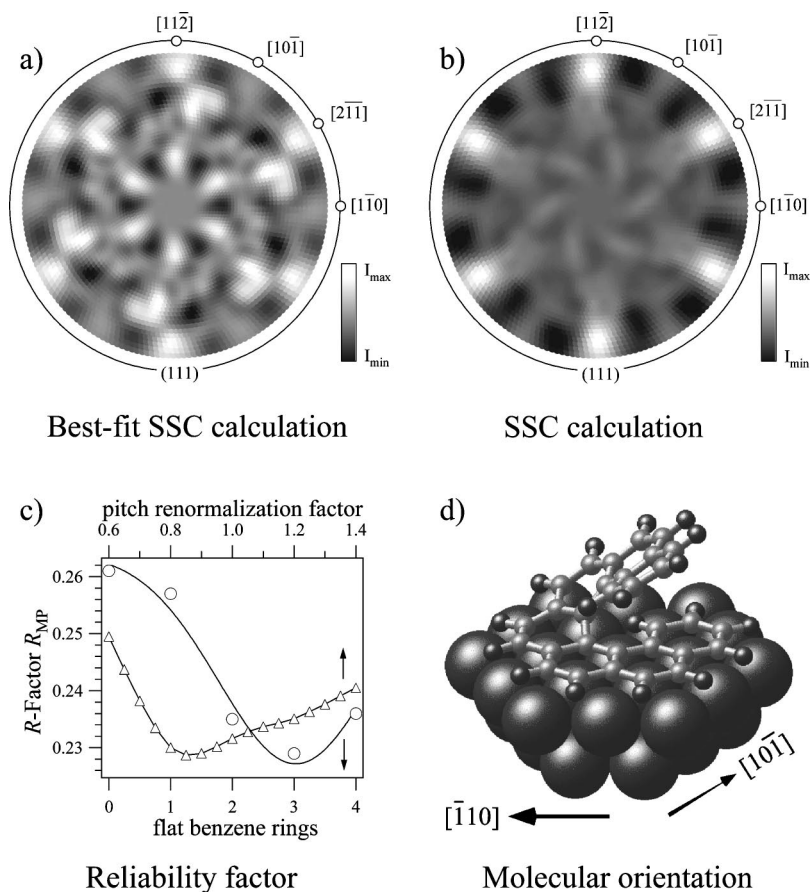


FIG. 4. (a) Best-fit single-scattering cluster XPD calculation, obtained for a *M*-heptahelicene molecule adsorbed with one terminal phenanthrene group (three C-6 rings) parallel to the Cu(111) surface. (b) Single-scattering cluster XPD calculation, obtained for a *M*-heptahelicene molecule adsorbed with its first C-6 ring parallel to the Cu(111) surface. (c) Dependence of the agreement between experiment and SSC calculations (R -factor) on the number of C-6 rings being coplanar to the substrate surface (circles) and on the pitch renormalization factor (triangles), respectively (see the text for details). (d) Schematic drawing of the molecular orientation of *M*-heptahelicene on the Cu(111) surface, as determined in the present work. Due to the sixfold rotational symmetry of the first Cu(111) surface layer, the helicene molecules take six azimuthal orientations related by subsequent rotations of 60° .

allow the molecule to adapt its molecular geometry (pitch) to the potential experienced upon adsorption on the Cu(111) surface.

The best-fit SSC calculation after the optimization of all parameters—the number of C-6 rings oriented parallel to the surface plane, the azimuthal orientation and the molecular pitch of the *M*-heptahelicene molecule (see Fig. 3)—is shown in Fig. 4(a). Unlike the best-fit calculations for all the other conformations that we tried, the pattern shown in Fig. 4(a) reproduces the main features of the experimental diffraction pattern [Fig. 2(a)] quite well (R -factor of 0.229). In particular, the wheel-type feature close to the center of the plot as well as the six intensity maxima at grazing emission angles are reproduced. The fact that the agreement is not as perfect as in the case of C_{60} on the same surface¹⁶ is not unexpected given the many more degrees of freedom in the present case. Note that in the case of C_{60} , the only degrees of freedom to consider are the three Eulerian angles describing the orientation of the molecule with respect to the surface. In the present case of the heptahelicene molecule with the assumption of a rigid molecular skeleton not being valid, the internal molecular conformation has to be optimized in addition to the orientation of the molecule. Moreover, the vibrational degrees of freedom of the molecule were treated in a simple Debye–Waller-type fashion, the limitations of which are well known.²⁸ The rather simple molecular mechanics geometry optimization calculations that we used and the simple renormalization of the molecular pitch are not expected to result in a perfectly adequate molecular confor-

mation, but in one that catches the essential features of the molecular conformation and orientation of the molecule when adsorbed on the Cu(111) surface. The level of agreement between the best-fit SSC calculation [Fig. 4(a)] and experiment [Fig. 2(a)] that we find (R -factor of 0.229) strongly suggests that this has been efficiently achieved.²⁹

As an example for the SSC calculations resulting from other molecular conformations, the best-fit SSC calculation for a heptahelicene molecule with its terminal C-6 ring confined in a planar configuration is given in Fig. 4(b). This calculation clearly does not reproduce even the most prominent features of the experimental pattern, which is reflected in the R -factor of 0.257.

The dependence of the R -factor on the number of C-6 rings being parallel to the surface and on the pitch renormalization factor are given in Fig. 4(c). Finally, a geometry is deduced where the molecule is adsorbed with three terminal C-6 rings (i.e., its terminal phenanthrene group) oriented parallel to the surface plane, and the molecular pitch is reduced by 12% (pitch renormalization factor 0.88) with respect to the conformation obtained from the MM+ molecular mechanics geometry optimization (i.e., three planar terminal rings without substrate interaction). We believe this smaller pitch to reflect the reduction in steric repulsion between the two ends of the molecule due to the bonding interaction with the Cu(111) surface. A perspective view of the molecular conformation and orientation of the *M*-heptahelicene molecule adsorbed on Cu(111) as determined here is given in Fig. 4(d).

Studies of planar aromatic hydrocarbons (e.g., benzene, naphthalene, coronene, 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.^{30,31} There are other examples, however, 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 nearly parallel to the surface normal.³² Furthermore, the molecular orientation may also depend on coverage or temperature.^{33,34} Adsorption with the ring plane parallel to the surface is usually explained by the assumption that the bonding to the substrate is provided by the π -orbitals of the aromatic rings. In close-packed monolayer structures, however, the intermolecular π - π -interactions in combination with an overall decrease of the surface energy due to high adsorbate coverage may become the driving force for a rearrangement away from a parallel adsorbate geometry. Note that this picture is only valid for aromatic hydrocarbons without further functional groups at the ring (e.g., benzoic acid or phenol) or heteroatoms in the ring (e.g., pyridine); these may strongly influence the adsorption geometry, even at low coverages.³³⁻³⁵

In the present case of heptahelicene adsorption on Cu(111), the molecule apparently seeks maximum overlap of its π -states with electronic states of the substrate surface, which is obtained when as many C-6 rings as possible are aligned along the surface plane. Due to steric repulsion between its two ends, however, the molecule has to spiral away from the surface after a certain number of flat C-6 rings. On Cu(111), the optimum energy balance between these two contrary trends is apparently found for a configuration with three C-6 rings flat on the surface and successive spiraling away up to a height of 3.1 Å.³⁶ We find the helicene molecules to take six different azimuthal orientations—the particular orientation shown in Fig. 4(d) and all those obtained from it by $n \times 60^\circ$ rotations—reflecting the sixfold rotational symmetry of the first Cu(111) surface layer. Note that the molecule–substrate registry shown in Fig. 4(d), in which we located the terminal C-6 ring on the surface on-top of a copper atom, is arbitrary; i.e., we cannot determine it from the present study.

HEPTAHELICENE ON Cu(332): EXPERIMENTAL RESULTS AND DISCUSSION

The Cu(332) surface consists of 12 Å wide (111) terraces separated by monoatomic steps running along the $[1\bar{1}0]$ direction. Given the molecular dimensions and assuming a similar adsorption geometry as derived above for Cu(111), the (111) terraces of the Cu(332) surface are expected to accommodate only a single heptahelicene molecule in the direction perpendicular to the steps even at saturated monolayer coverage. Motivated by the speculation that a specific step–molecule interaction might energetically favor one of the six azimuthal orientations observed on the Cu(111) surface, we expanded our study to the *M*-heptahelicene on Cu(332) system.

The experimental C 1s XPD pattern from a 1/3 ML coverage film of *M*-heptahelicene on Cu(332) is shown in Fig.

5(a). Apart from removal of the smooth polar-angle-dependent background typical for adsorbate emission, the pattern represents raw data. In contrast to the sixfold rotational symmetry observed in the C 1s XPD pattern from *M*-heptahelicene on Cu(111), the pattern shown in Fig. 5(a) exhibits only C₁ rotational symmetry. Furthermore, the intensity distribution within the diffraction pattern directly reflects the helical structure of the *M*-heptahelicene molecule. These observations show unambiguously that the confinement of the molecules onto narrow terraces and the concurrent step–molecule interaction lead to a unique azimuthal orientation of the *M*-heptahelicene molecules. Furthermore, the local orientation of the molecule and its molecular conformation on the Cu(332) surface is the same as the one found for the Cu(111) surface! This follows from a simple comparison of the corresponding diffraction patterns: if apart from the difference in the number of different azimuthal orientations the molecules adsorb identically on the (111) terraces of Cu(332) and on the native Cu(111) surface, the corresponding XPD patterns should be related by a rotation of 10° around the $[1\bar{1}0]$ axis oriented in the surface plane parallel to the steps³⁷ and sixfold azimuthal averaging around the $[111]$ direction. The “simulated” pattern shown in Fig. 5(b), obtained from the heptahelicene/Cu(332) pattern in Fig. 5(a) by a 10° rotation around¹⁻¹⁰ and subsequent sixfold averaging around $[111]$, agrees well with the experimental heptahelicene Cu(111) pattern [Fig. 2(a)]. This clearly proves that on the (111) terraces of Cu(332) the heptahelicene molecule takes the same molecular conformation and orientation as on the Cu(111) surface.

It remains to determine which one of the six azimuthal orientations coexisting on Cu(111) is the one favored by the molecule–step interaction on Cu(332). We find that the second and third planar C-6 rings on the terraces are aligned along the step edges, resulting in the arrangement schematically shown in Fig. 5(d). The intramolecular C–C directions for this configuration are stereographically plotted in Fig. 5(c), where each spot corresponds to one of the 30×29 C–C directions with a spotsize that scales with the inverse C–C distance. These spots indicate the expected locations of forward focusing intensity enhancements in the diffraction pattern. Although in this purely geometrical picture relative intensities are not expected to be accurately predicted, the resulting plot [Fig. 5(c)] clearly explains the particular (helical) asymmetry of the intensity distribution observed in the experimental pattern [Fig. 5(a)],³⁸ thus confirming the configuration shown in Fig. 5(d).

We conclude that the *M*-heptahelicene on a Cu(332) system represents a chiral surface with single-phase orientational order. This “in-phase” orientation of the molecules might be particularly relevant for the nonlinear optical response of the monolayer, and will be the subject of forthcoming second-harmonic generation (SHG) studies. It will be interesting to see to what extent the SHG signal depends on the degree of molecular order of heptahelicene on Cu(111) and Cu(332).

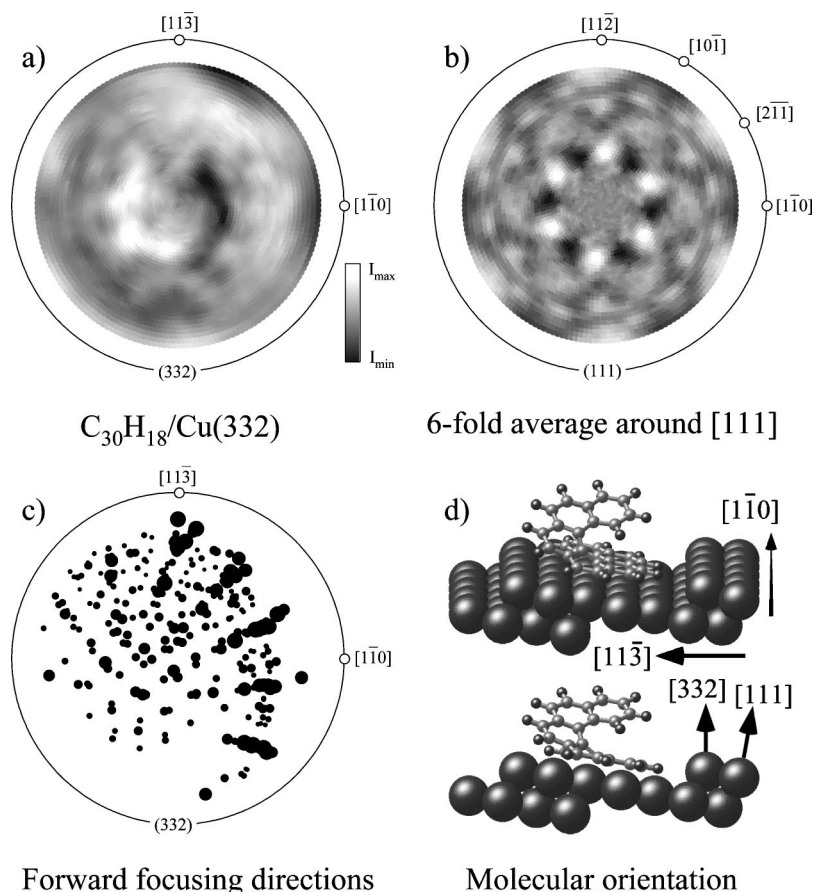


FIG. 5. (a) An angle-scanned x-ray photoelectron diffraction pattern for C 1s emission from the *M*-enantiomer of heptahelicene on Cu(332). The handedness of the molecule is directly reflected in the diffraction pattern. (b) The "simulated" diffraction pattern, obtained by sixfold rotational averaging of the pattern in (a) around the $[111]$ direction, is almost identical to the experimental pattern from heptahelicene on Cu(111), indicating the same molecular conformation on both surfaces. (c) The stereographic plot of the interatomic C-C directions (forward-focusing directions) within a *M*-heptahelicene molecule oriented as shown in (d) clearly explains the intensity distribution of the experimental pattern (a). The spotsize is inversely proportional to the corresponding C-C distance, thus mimicking the strength of the forward-scattering intensity enhancement expected at the corresponding emission angle. (d) Schematic drawing of the molecular orientation of the *M*-isomer of heptahelicene on the Cu(332) surface. The molecule-step interaction confines the molecule to the particular azimuthal orientation shown.

CONCLUSIONS

We have determined the molecular conformation and orientation of the *M*-enantiomer of heptahelicene on the Cu(111) and Cu(332) surfaces. On both surfaces, the molecules are found to adsorb in a geometry with their terminal phenanthrene group (the first three C-6 rings) oriented parallel to the (111) faces and to successively spiral away from the surface from the fourth ring on. Whereas on Cu(111) the coexistence of six azimuthal molecular orientations is determined, on Cu(332) the step-molecule interaction leads to a unique azimuthal alignment of the heptahelicene molecules. The *M*-heptahelicene on Cu(332) adsorbate system thus represents a chiral surface with single-phase helical orientational order.

ACKNOWLEDGMENT

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