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Transfer of chirality from adsorbed chiral molecules to the substrate highlighted by circular dichroism in angle-resolved valence photoelectron spectroscopy

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Studies of self-assembled chiral molecules on achiral metallic surfaces have mostly focused on the determination of the geometry of adsorbates and their electronic structure. The aim of this paper is to provide direct information on the chirality character of the system and on the chirality transfer from molecules to substrate by means of circular dichroism in the angular distribution of valence photoelectrons for the extended domain of the chiral self-assembled molecular structure, formed by alaninol adsorbed on Cu(100). We show, by the dichroic behavior of a mixed molecule–copper valence state, that the presence of molecular chiral domains induces asymmetry in the interaction with the substrate and locally transfers the chiral character to the underlying metal atoms participating in the adsorption process; combined information related to the asymmetry of the initial electronic state, which is expected to be chiral, and the final electronic state, which locally probes the asymmetry of the potential, has been obtained. Identification of chirality in the adsorption footprint sheds new light on the transfer of chirality from a chiral modifier to a symmetric metal surface and represents an important aspect for controlling and tuning the functionality of the molecule–metal interfaces.

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I. INTRODUCTION

In recent years, the study of two-dimensional (2D) chiral systems has been motivated mainly by their potential role in the heterogeneous asymmetric catalysis.[1–5] The chiral modification of achiral metal surfaces, based on self-assembled adsorbed chiral molecules, is a promising method to produce well-defined, catalytically active chiral sites on solid surfaces.[6,7] These efforts focus mainly on the determination of the adsorption geometry and its relationship to the molecular handedness by means of scanning tunneling microscopy (STM), reflection absorption infrared spectroscopy, temperature-programmed desorption, electronic spectroscopies like x-ray photoelectron, and theoretical model calculations.

The adsorption process of chiral molecules might lead to the appearance of chiral electron states from the bonding of the molecules to the underlying surface atoms. Understanding of the new chiral bondings—in other words, the birth of a chiral footprint in the substrate—is important for understanding which surface properties are sensitive to molecular chirality in terms of controlling the capability of chiral molecules to self-organize in chiral domains and opening the way for investigation of 2D chiral amplification in molecule–surface systems.[8,9] In describing the chiral properties of the self-assembled monolayer (SAM), it is also important to consider the molecular handedness needs to take into account the chirality transfer through the substrate and a manifestation of chirality in the form of the adsorption footprint.[9,10]

Determining how this additional chiral feature is correlated to the electronic states originating from the molecule bonding to the underlying metal atoms of the surface is a challenging task. Investigation of the chiral properties of the molecular overlayer and of the newly appeared chiral interface states using specific dichroic spectroscopies would be of great value. Conventional techniques based on polarized optical absorption and circular dichroism on molecular monolayers present severe difficulties due to the low intensity of both absorption and dichroic signals. By contrast, circular dichroism in the angular distribution (CDAD) of photoelectrons can be usefully applied to study molecular adsorbates on surfaces. Theoretical calculations are able to predict CDAD of photoelectrons for randomly oriented free chiral molecules,[11–13] experimentally confirmed in the gas phase, for both core and valence electronic states.[14–18] Increasing complexity is expected in the case of molecules adsorbed on surfaces due to the influence of experimental geometry that may induce dichroic signals unrelated to the chiral properties of the 2D molecular system; nonchiral surfaces can give rise to a significant CDAD signal if the geometry of the experiment is chiral, i.e., if the plane defined by the outgoing photoelectrons' direction and incoming circularly polarized photons is not a symmetry plane of the system.[19–21] It has been shown that a strong CDAD signal is observed for CO adsorbed on Pd(111), but this dichroism can be suppressed by performing the experiment in a surface symmetry plane.[20,22] Few published papers used CDAD to investigate the chiral character of the electronic states of 2D chiral molecular systems, and they focused on the study of the carbon core level photoemission of small chiral molecules adsorbed on surfaces, namely, alanine on Cu(110) and 2,3-butanediol on Si(100).[23–25] These authors investigated the photoemission of the C 1*s* state to chemically localize the chirality of the adsorbed molecule; in so doing, they carefully defined the geometry of the experiment and demonstrated that CDAD due to chirality of the adsorbate can be distinguished from that due to spurious geometric effects if the photoelectrons and photons directions are on a symmetry plane of the substrate.

In this work, we extend investigations to the valence states by measuring CDAD of the valence photoelectrons as a function of photon energy and photoelectron emission angle for a 2D chiral alaninol SAM, assuming that molecular valence states all carry chiral characters derived from the asymmetric molecular potential. We show that CDAD effects extend for a large portion of the photoelectron valence spectrum, in addition to a mixed metal–molecule bond formed between the $3d$ copper and amino-derived $2p$-like molecular states, as derived from comparison to previous photoelectron results[26] and published calculations.[27] The latter mixed signal might then be a direct probe of a local chirality transfer from the molecule to the underlying copper surface atoms.

Alaninol adsorbed on Cu(100) is a suitable system because it shows an extended chiral domain of a self-assembled molecular structure.[26–30] Alaninol is a small and conformationally flexible bifunctional chiral amino-alcohol belonging to a group of molecules important as industrial precursors or intermediates in the synthesis of pharmaceutical compounds.[31] It is known that D- and L-alaninol adsorb on a Cu(100) surface, forming an ordered self-assembled chiral monolayer.[26,28,29] At room temperature (RT), D-alaninol shows a $(4\ {-1},\ 1\ 4)$ molecular superstructure rotated clockwise and L-alaninol shows a $(4\ 1,\ {-1}\ 4)$ molecular superstructure rotated counterclockwise by 14° with respect to the [011] Cu direction; the 2D unit element of the superstructure is formed by four molecules, arranged in a tetramer.[27,30,32]

II. EXPERIMENTS

The CDAD experiments were performed by using circularly polarized radiation available at the Advanced Photoelectric Effect (APE) Experiments beamline of the ELETTRA Synchrotron Radiation Facility (Trieste, Italy). Angle-resolved photoelectron spectra of the valence band (VB) were measured with a Scienta 2002 spectrometer equipped with 2D detector with angular acceptance of 14°. The angle between the incoming photons and the axis of the electron analyzer is fixed at 45°. The experimental arrangement is sketched in the inset of Fig. 1, where $\vec{\mathbf{k}}$ and $\vec{\mathbf{q}}$ are the directions of photoelectrons and incident light, respectively, and $\vec{\mathbf{n}}$ is the surface normal. All experiments were performed at RT, maintaining the scattering plane defined by the [011] direction and the surface normal; alignment of the Cu(100) crystal was obtained measuring a null dichroic signal from the clean copper surface. A_{CDAD} data in Fig. 3 were obtained by summing the photoelectron spectra in a range of 4° (±2°) around the nominal angle. The total instrumental resolution of the measurements was 20 meV.

The Cu(100) surface was cleaned by repeated cycles of Ar^+ sputtering (600 eV) and annealing (700 K). The two enantiomers of alaninol ($\mathrm{NH_2\text{-}CH(CH_3)\text{-}CH_2OH}$, 99.9% purity, having opposite chirality), D- and L-alaninol, contained in glass tubes, were purified with several freeze–pump cycles. To obtain the two chiral surfaces, the vapors of each enantiomer of alaninol were introduced separately into the ultra-high-vacuum chamber through leak valves while the Cu(100) was held at RT. A saturated SAM (1 monolayer, or ML) was obtained at exposures of ~15 Langmuir (L) of each enantiomer (1 L is the exposition at 1.33×10^{-4} Pa for 1 s).[26]

The asymmetry coefficient A_{CDAD} is defined as

$$A_{\mathrm{CDAD}} = \frac{I_{\mathrm{RCP}} - I_{\mathrm{LCP}}}{I_{\mathrm{RCP}} + I_{\mathrm{LCP}}}$$

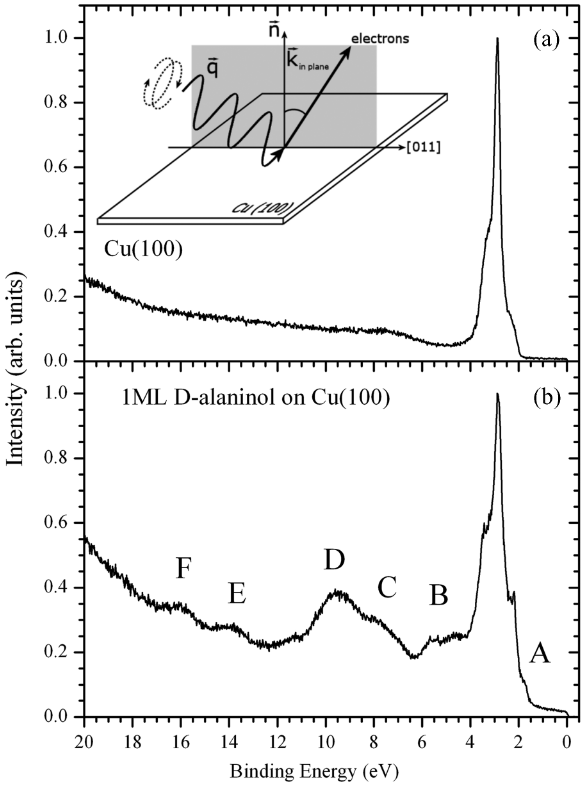

FIG. 1. Photoelectron VB spectra (sum over LCP and RCP light) obtained at (a) normal emission ($h\nu = 30$ eV) for clean Cu(100) and (b) 1 ML of D-alaninol adsorbed on Cu(100) at RT. Labels A to F indicate peaks attributed to alaninol. The inset in panel (a) shows a sketch of the experimental geometry ($\vec{\mathbf{k}}$ and $\vec{\mathbf{q}}$ are the directions of the photoelectrons and of the incident light, respectively, and $\vec{\mathbf{n}}$ is the surface normal).

Where I_{RCP} and I_{LCP} are the intensities of signals in the VB photoelectron spectrum obtained with right and left circularly polarized (RCP and LCP) light, respectively. The values of the A_{CDAD} coefficients, reported in Fig. 3, are the intensity ratios of the features appearing in the difference spectrum [$I_{\mathrm{RCP}} - I_{\mathrm{LCP}}$, Fig. 2(a)], taken at each peak in the VB spectrum (labeled A, B, C, etc.) and normalized to the sum of the RCP and LCP light ($I_{\mathrm{RCP}} + I_{\mathrm{LCP}}$) spectra after subtraction of the background of the secondary electrons. The error bars reported in Fig. 3 were evaluated from the noise spread occurring in the measured spectrum around the selected peak position and propagated for the calculation of the A_{CDAD}.

III. RESULTS AND DISCUSSION

Figure 1 reports the VB photoelectron spectrum obtained at normal emission with 30 eV of photon energy for 1 ML of D-alaninol adsorbed on Cu(100) [Fig. 1(b)] and clean Cu(100) [Fig. 1(a)]. The signature of the ordered alaninol monolayer on the Cu(100) surface is shown by the presence, in Fig. 1(b), of several peaks at binding energy (BE) of 1.75, 5.0, 7.7, 9.7, 13.9, and 16.0 eV (A to F). These structures have been identified recently by comparison of valence and core photoelectron spectra obtained as a function of molecular coverage of the surface and assigned by density functional theory (DFT) calculations.[26,27,32] The calculated valence electron states, supported by the results from core level spectroscopy, indicate the copresence of two possible configurations for adsorbed alaninol molecules and show the formation of a chemical bond between molecule and substrate.[27]

The photoelectron spectral features found on the lower and higher BE sides of the Cu 3*d* electronic states peak were identified as being due to the antibonding state (peak A) and the bonding state (buried in peak B), respectively, originating mainly from the interaction of the Cu 3*d* states of the two copper atoms directly involved in binding with the amino group in a bridge geometry and involving the nitrogen-derived $2p$-like lone pair state of the alaninol molecule; the electronic density distribution associated with these electron states, reported in Fig. 7 of the paper of Gori *et al.*, shows the spatial distribution of mixed orbitals.[27] The calculations report that these states are the results of a strong interaction between alaninol and copper occurring after a dehydrogenation process at the amino group due to adsorption process, following the Newns–Anderson model applied to adsorbates on metal surfaces with d bands. Localized electronic states close to transition metal 3*d* orbitals are well known to be formed in presence of a strong interaction between adsorbate and nearest-neighbor substrate metal atoms. If the interaction is strong enough or the apparent *d* band width is narrow enough, then localized states appear outside the *d* band; the chemisorption energy of the bond is related to the energy shift of the adsorbate electronic level and to the width of the formed surface state.[33,34] In the BE range from 5 to 11 eV, further structures are found (B to D), associated with molecular orbitals arising mainly from interaction of C, N, and O $2p$ orbitals and spread over the entire molecule. Peaks at binding energies higher than 13 eV [E and F in Fig. 1(b)] originate mainly from C, N, and O $2s$ electrons.[27] The angle-resolved analysis of these electronic states, using linearly polarized radiation and in the limit of our energy and angular resolutions, does not show any energy dispersion along $\bar{\Gamma} - \bar{X}$ or $\bar{\Gamma} - \bar{M}$ lines or in the direction of the main symmetry of the molecular overlayer (14° off $\bar{\Gamma} - \bar{X}$), indicating a localized nature of these electronic states.

Figure 2 reports the RT valence photoelectron spectra for 1 ML of D-alaninol [Fig. 2(b)] and L-alaninol [Fig. 2(c)] enantiomers adsorbed on Cu(100) taken at normal emission with 30 eV of photon energy using RCP and LCP light. The difference between the photoelectron intensities obtained with RCP and LCP light for L-alaninol and that for D-alaninol, i.e., the dichroic spectrum, are reported in Fig. 2(a) as blue (dark gray) and red (light gray) solid lines, respectively, and show features in close correspondence with the previously outlined valence photoelectron structures. Low-energy electron diffraction (LEED) patterns [insets in Figs. 2(b) and 2(c)] show (4 −1, 1 4) or (4 1, −1 4) molecular superstructures rotated clockwise or counterclockwise, respectively, by 14° with respect to the Cu [011] direction. The LEED results and the STM images demonstrate the ability of alaninol to form a single long-range chiral domain producing global chiral surfaces of opposite chirality by evaporating separately the two alaninol enantiomers on the Cu(100) surface.[26,28,29]

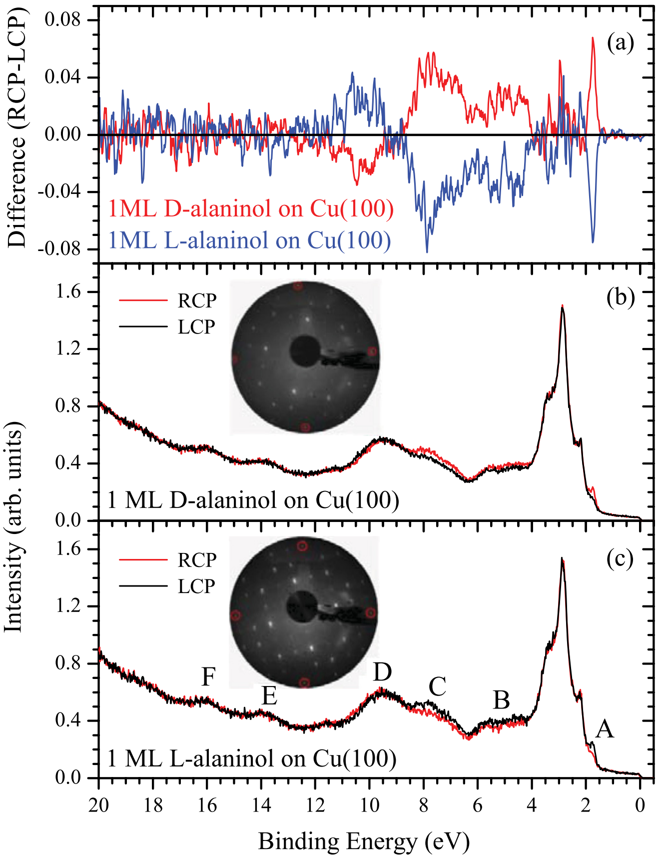

FIG. 2. (Color online) Circular dichroism in the valence photoelectron spectra for alaninol adsorbed on Cu(100) (RT, normal emission, $h\nu = 30$ eV). (a) The difference (RCP − LCP) for L-alaninol and that for D-alaninol are reported as blue (dark gray) and red (light gray) solid lines, respectively. Valence photoelectron spectra for (b) D-alaninol and (c) L-alaninol obtained with RCP (red/light gray solid line) and LCP (black solid line) light. The insets show the LEED patterns of 1 ML of (b) D-alaninol and (c) L-alaninol; red circles indicate the diffraction spots due to Cu(100).

The reported difference spectra, for 1 ML of L- and D-alaninol on Cu(100), present mirror image behavior. This result clearly proves that dichroic signals originate only from the chiral nature of the alaninol–copper system and wipes out any doubt about the correctness of the experimental configuration or the possibility of spurious chiral effects from experimental geometry.[20] A CDAD experiment performed in such a way that the plane containing the incident photons, the surface normal, and the detector coincide with a mirror plane of an achiral surface will yield no dichroic signal. When a chiral molecule is deposited on the surface, the CDAD signal should appear because the mirror plane is lost. Therefore, within the substrate mirror plane, the measured CDAD is a direct consequence of the chirality of the adsorbed molecule, validating CDAD to discriminate and characterize the chiral properties of the valence electronic states of this system. An achiral adsorbate adopting a low-symmetry configuration on the surface can create locally the loss of the plane of symmetry, but in this case the surface remains globally achiral and the experiment will average over equally probable domains related by the missing mirror plane, producing a null CDAD signal.

Only a few of the VB orbitals present dichroic effects at 30 eV of photon energy. Values of the A_{CDAD} of 0.15 ± 0.01, 0.05 ± 0.01, 0.08 ± 0.01, and -0.05 ± 0.01 were found for the peaks labeled A to D. Values close to 0 for A_{CDAD} were obtained for peaks E and F. Negligible values were obtained in the Cu 3*d* BE range (2–4 eV).

Assignment of valence electronic states in the photoelectron spectrum could be difficult because of overlapping due to their close BE positions. The shape of the dichroic spectrum allows better definition of the contributions from alaninol–Cu interactions to the valence photoelectron features in energy regions where their overlap does not allow sufficient energy discrimination. Figure 2(a) makes it possible to assign the B to E peaks to different electronic states, because their dichroic signals are different in intensity and shape. Dichroism is clearly recognized in the high BE side of peak D, showing the contribution of a molecular state to the VB; moreover, this peak shows the opposite sign in dichroic behavior with respect to the others. The difference in sign indicates that peaks B and C originate as the sum of electronic states with different symmetries. The effect of disentangling is particularly useful for peak A, because it is buried below the tail of Cu 3*d* states, while in the difference spectrum, a narrow peak of 240 meV at full width at half maximum (FWHM) is observed. This value is comparable with that obtained by Kera *et al.* for the highest occupied molecular orbital (HOMO) band in the VB spectrum of copper–phthalocyanine on graphite; at RT, they measured a HOMO band formed by three vibrationally resolved peaks (FWHM = 172 meV).[35] The value of the HOMO bandwidth can be used to understand phenomena at the organic–inorganic interfaces and therefore tune the molecular devices properties because it is related, through the lifetime of the photogenerated HOMO hole, to the charge transport properties across the molecule–substrate interface.[35,36] The small bandwidth value of peak A reflects the high degree of localization of the orbital and a long lifetime for the HOMO hole.

The dynamic effect on the A_{CDAD} dichroic parameters in the VB spectrum has been studied as a function of the photon energy (at normal emission) and of the photoelectron emission angle (at fixed photon energy). Figure 3 reports the dispersion of A_{CDAD} values in the ranges of 25 to 42 eV of photon energies and −4° to 34° for electron emission angles. As a general trend, we observed smooth changes in the A_{CDAD} values as a function of the photon energy. A clear dynamic effect can be seen for peaks A to D in the A_{CDAD} measured as a function of the photon energy, while no dichroic effect is measured for peaks E and F. Dynamic effects of valence states in the CDAD photoelectron spectroscopy have been recently studied for alaninol in the gas phase from experimental and theoretical points of view.[37] The average sizes of the A_{CDAD} parameter found for alaninol adsorbed on Cu(100) are higher than those measured for valence states in free alaninol[37] and for C 1*s* in molecules adsorbed on surfaces such as alanine on Cu(110) and 2,3-butanediol on Si(100).[23–25]

In Fig. 3(b), we present the angular dependence, in the scattering plane [see the inset of Fig. 1(a)] of the dichroic parameter values. Modifications of the A_{CDAD} parameters for peaks A to E as a function of the polar electron emission angle are shown at 30 eV of photon energy (peak F has no dichroic signal). The peak A dispersion shows a maximum at normal emission and decreases monotonically, reaching zero at 10°. An inversion of the sign in the dichroic parameter is observed for peak B when it is ∼5°. Peak C dependence presents smooth changes and reaches zero at 34°, while peak D always remains negative without significant changes from −4° to 34°. Peak E shows null dichroism around 0° and negative values for angles higher than 5°.

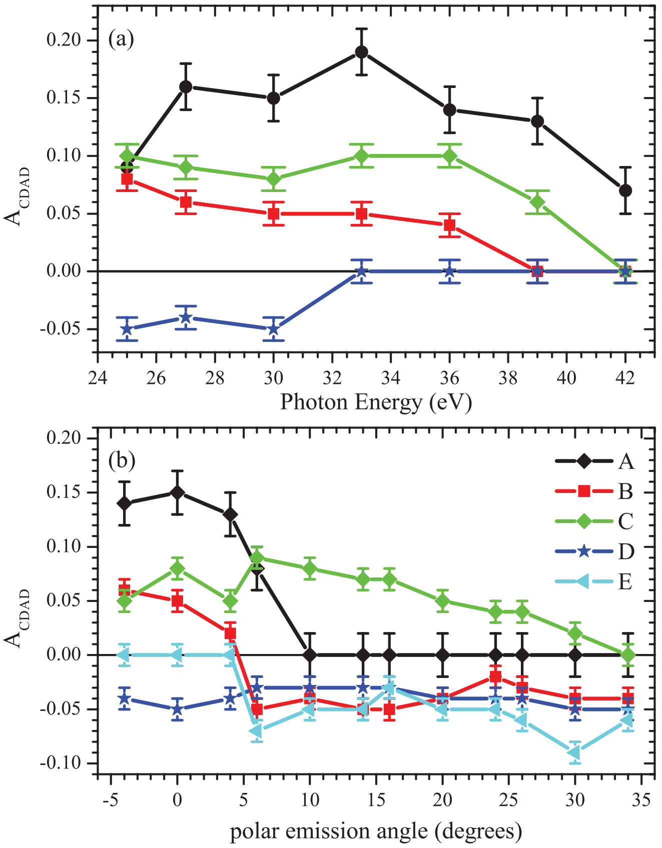

FIG. 3. (Color online) Circular dichroism (A_{CDAD}) in the photoelectron valence spectra for 1 ML of alaninol adsorbed on Cu(100) at RT measured in the scattering plane defined by the [011] surface direction and the surface normal [see inset of Fig. 1(a)]. A_{CDAD} for valence structures labeled in Figs. 1 and 2 measured as a function (a) of the photon energy in normal emission and (b) of the polar electron emission angle at 30 eV of photon energy. Valence structures E and F are not reported when a zero A_{CDAD} value is present.

The reported CDAD data show values up to 15% for valence molecular orbitals and allow disentanglement among different electronic levels by means of their dichroic nature. Different behavior of the A_{CDAD} parameters associated with different electronic orbitals in the VB as a function of the photon energy and photoelectron emission angle has been observed, showing the ability of the A_{CDAD} parameter to highlight the chiral features of a self-assembled 2D structure. The A_{CDAD} parameter is also sensitive to the chiral character of the valence electronic states depending on the symmetry of the initial states; orbitals with a predominant π character (A to D) present, on average, larger amplitudes of the dichroic signals when compared with states with a predominant σ character (E and F).[27]

We obtained direct information on chirality sharing between an adsorbed chiral molecule and the surface atoms through the appearance of the CDAD signal related to the mixed alaninol–copper antibonding feature (peak A) originating from the strong interaction between alaninol and underlying copper atoms. Formally, the presence of an adsorbed chiral molecule renders the whole surface chiral, because even the substrate atoms close to the adsorbate have a local environment for which there is no mirror equivalent. As already discussed in the introduction, in this case, the CDAD signal related to the chiral character of the molecule–surface interaction can be observed using appropriate experimental geometry.[23–25] This effect may be expected to be seen from any of the constituent atoms of the adsorbed molecule, and in principle, it could be seen in the photoelectron signal from the substrate atoms. The detection of a CDAD signal from substrate atoms would open the possibility to study the chirality in the proximity of the surface and then to have direct information on the chirality transfer from the molecule, although the CDAD signal is probably very weak, because only a small portion of the detected substrate photoelectron signal comes from atoms sufficiently close to the adsorbed molecules to be influenced by their presence.

The presence of a mixed alaninol–copper state found in the VB overcomes this sensitivity problem for CDAD and makes possible the study of the chirality transfer from adsorbed chiral molecules to the surface through the copper atoms in interaction with the molecule; moreover, the photoelectrons coming from this electronic state are localized close to the bond. It is well known that the sign and the magnitude of the CDAD signal, related to the irreducible representation of the point group of the overall adsorption system (chiral molecule and copper atoms), is proportional to the dipole matrix element due to the electronic transition from the initial state into the continuum of final states.[12,13] In our case, the CDAD signal observed for electrons photoemitted from the mixed alaninol–copper state at peak A is expected to be due to both initial and final states that are asymmetric due to the interaction of alaninol with the surface that locally renders chiral the potential. The electronic initial state is expected to be chiral because it can be considered a sum of chiral valence states of alaninol and achiral states of copper. The final electronic state (also sensitive to the underlying copper atoms participating in the adsorption process) locally probes the asymmetry of the potential in which the photoelectrons move. In the case of chiral molecules on surfaces, the capability of CDAD for a symmetric $1s$ core initial state to probe the asymmetry of the final state and to locally study the chirality of the system has been proven (i.e., CDAD from core levels is caused by the anisotropic environment of the emitter atoms).[23–25] Even if the relative importance of initial and final states is unknown, the CDAD signal of the hybridized interface state at peak A provides direct spectroscopic proof of the transfer of chirality from alaninol to the bounded copper atoms underneath the molecule. Moreover, it is known from optical spectroscopy of classic coordination compounds that d states from a central metal ion acquire chirality when surrounded by a dissymmetric charge distribution belonging to a chiral or a prochiral molecule.[18,38] In addition, the angular dependence of peak A dichroism is more localized around the surface-normal direction and shows higher average values in comparison to the other valence orbitals. No CDAD signal is observed for the copper d band. The signals of the d band originate not only from surface copper atoms that are not directly connected to alaninol but also, considering the electron mean free path, from copper atoms of deeper layers. For this reason, related to a sensitivity problem, we cannot state that the other surface copper atoms are unable to detect asymmetric potential due to the presence of alaninol.

Full understanding and characterization of the chiral transfer process require modeling of the alaninol–Cu(100) interface. Major theoretical efforts have been directed toward the dichroic study of gas phase chiral molecules, and good agreement with experimental results has been obtained.[15] Moreover, it has been shown that molecular geometry (the difference in the conformer distribution, in the vibrational content, or in the rotation of a molecule portion, e.g., CH_3) is important to obtain correct A_{CDAD} parameters.[37,39,40] The high sensitivity of the CDAD signal to the change in the system geometry means the coordinates of the atoms composing the surface unit cell should be known with low error to have reliable results from the calculations. At the moment, mostly due to the complexity of the unit cell and the flexibility of alaninol, the best geometry obtained by recent combined DFT and molecular dynamics calculations on this system was able to simulate the STM image of the unit cell describing the chirality changes of the surface as a function of the alaninol amount on the surface. However, shortcomings in the description of the details of the protrusion found in the experimental STM image show that we need better geometry.[29]

IV. CONCLUSIONS

We have investigated, using circular dichroism in the angle distribution of valence photoelectrons, the chiral electronic features of the extended 2D domain of a chiral self-assembled molecular structure originating from the adsorption of L- and D-alaninol on Cu(100). The A_{CDAD} parameters, which are related to the chirality of each valence orbital of the molecule–surface system, have been measured, and it has been found that their magnitude depends on the photon energy and electron emission angle (up to 15%) and on the predominant character of the initial electronic states (π or σ). A_{CDAD} is shown to be a sensitive tool to disentangle the chiral electron contribution into the overlapping VB largely representative of the achiral electronic states of the substrate. Information on the chirality transfer from the adsorbed chiral molecules to the underlying atoms of the achiral surface has been obtained through analysis of the dichroic signal originating from the antibonding alaninol–copper orbital formed in the chemisorption process. The CDAD signal from this hybridized interface state furnishes combined information related to the asymmetry of the initial electronic state, which is expected to be chiral, and the final electronic state, which locally probes the asymmetry of the potential in which the photoelectrons move.

Although theoretical calculations are highly desirable for deeper insight, we believe that the study of CDAD experiments applied to molecule–substrate valence orbitals is a useful and unique direct tool for the identification of the chiral character in the adsorption footprint, allowing control of the functionality of the molecule–surface interfaces.

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