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# Circular dichroism in angle resolved valence photoelectron spectroscopy highlights the transfer of chirality from adsorbed chiral molecules to the substrate

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**Abstract**

The study of self-assembled chiral molecules on achiral metallic surfaces is mostly focused on the determination of the geometry of adsorbates and the related 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 the substrate by means of circular dichroism in the angular distribution of valence photoelectrons for extended domain of chiral self-assembled molecular structure, formed by alaninol adsorbed on Cu(100). We show that the presence of molecular chiral domains induces chiral electronic states in the interaction with the substrate and locally transfers chiral character to the underneath metal atoms participating in the adsorption process. Identification of chirality in the adsorption footprint represents an important aspect for controlling and tuning the functionality of the molecular-metal interfaces.

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 surface.[6,7] These efforts focus mainly on the determination of the adsorption geometry and its relationship to the molecular handedness by means of electronic spectroscopies and scanning tunneling microscopy (STM) together with theoretical modeling approaches.

The adsorption process leads to a transfer of the chirality from the molecules to the underneath surface atoms. The understanding of the chiral transfer process, in other words the chirality footprint in the substrate, is important with respect to the open question related to which of the surface properties are sensitive to molecular chirality and to control the capability of chiral molecules to self-organize in chiral domains opening the way for a 2D chiral amplification in the molecule/surface systems. [8,9] In this respect, the investigation of the chiral properties of the molecular overlayer and its chirality transfer 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 level of both absorption and dichroic signal intensities. By contrast, circular dichroism in the angular distribution (CDAD) of photoelectrons (PE) 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,[10-12] experimentally tested in gas phase for both core and valence electronic states.[13-16] In the case of molecules adsorbed on surfaces, further complications are expected because of additional effects due to the experimental geometry that may induce dichroic signal completely unrelated to the chiral properties of the 2D molecular system; non chiral 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.[17-19] Few published papers used CDAD to investigate the chiral character of the electronic states of 2D molecular chiral systems and they focused on the study of the core level photoelectrons from chiral surfaces, obtained by the adsorption of small chiral molecules (alanine on Cu(110) and 2,3-butanediol on Si(100)).[20-22] In this way they succeed to correlate the dichroism of core level photoelectron peaks to the position of the chiral centers in the molecular net of the carbon atoms.

In this work we extend the previous studies on the core levels to the valence states by measuring the CDAD of the valence photoelectrons as a function of photon energy and photoelectron emission angle to identify the specific chiral states involved in the Cu-molecule

bonding and investigate the possible transfer of chirality from the adsorbed chiral molecules to the achiral surface through the electronic states participating in the adsorption process.

Alaninol adsorbed on Cu(100) has been chosen as a suitable system because it has been observed to form an extended domain of chiral self-assembled molecular structure.[23-27] Alaninol is a small and conformationally flexible bifunctional chiral amino-alcohol belonging to a group of molecules that are important industrial precursors or intermediates for the synthesis of pharmaceutical compounds.[28] It is known that D-alaninol and L-alaninol adsorbed on Cu(100) surface form an ordered self-assembled chiral saturated monolayer.[23-25] At room temperature (RT), D-alaninol (L-alaninol) shows a (4 -1, 1 4) (or (4 1, -1 4)) molecular superstructure rotated clockwise (or counterclockwise) by 14° with respect to the [011] Cu direction; the 2D unit element of the superstructure is formed by four D-alaninol molecules, arranged in a tetramer.[26,27,29]

The CDAD experiments were performed by using circular polarized synchrotron radiation available on the APE beamline at the ELETTRA storage ring of "Sincrotrone Trieste" (Italy). Angular resolved photoelectron spectroscopy of valence band (VB) was performed with a Scienta 2002 spectrometer equipped with 2D detector with angular acceptance of 14°. The angle between the incoming circular polarized photons and the axis of the electron analyzer is fixed at 45°. The experimental arrangement is sketched in the inset of Figure 1 where **k** and **q** are the directions of photoelectrons and incident light, respectively, and **n** is the surface normal. All the experiments have been 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 Figure 3 were obtained by summing up the photoelectron spectra in a range of 4° (±2°) around the nominal angle. The total instrumental resolution of the measurements was 20 meV.

High purity (99.999 %) Cu(100) single crystal was cleaned by repeated cycles of $Ar^+$ ion sputtering (at 600 eV) and annealing at 700 K to obtain a well-ordered Cu(100) surface, witnessed by both the sharpness of the low energy electron diffraction (LEED) spots and the absence of signals in the VB photoelectron spectra of clean Cu(100) due to surface contaminants. D-Alaninol and L-alaninol ($NH_2$-CH($CH_3$)-$CH_2OH$, 99% purity) were purified with several freeze-pump cycles and the vapors introduced into the ultra-high vacuum chamber through a leak valve while the Cu(100) was held at RT. Mass spectrometry was used to monitor the purity and integrity of the molecule during the exposition. The experiments were performed by exposing the Cu(100) surface to D-alaninol (or L-alaninol) until a saturated (1 ML, ML = monolayer) self-assembled molecular layer was obtained on the surface. A saturated surface was obtained, for both enantiomers, with exposures of about 15 L (1 Langmuir (L) defined as an exposure at $1.33 \times 10^{-4}$ Pa for one second).[23]

The asymmetry coefficient $A_{CDAD}$ is defined as

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

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

Figure 1b reports the valence band PE spectrum obtained at normal emission with 30 eV photon energy for 1 ML of D-alaninol adsorbed on Cu(100) at RT (sum of the spectra measured with LCP and RCP photons). The valence band spectrum of clean Cu(100), measured in the same experimental condition, is reported in Figure 1a. The inset depicts the experimental geometry.

The signature of the ordered alaninol monolayer on Cu(100) is shown by several peaks in Figure 1b at binding energy (BE) of 1.75 eV, 5.0 eV, 7.7 eV, 9.7 eV, 13.9 eV and 16.0 eV (labeled A to F). These structures have been characterized recently by comparison of valence and core photoelectron spectra obtained as a function of molecular amounts on the surface and density functional theory (DFT) calculations.[23,26,29] The valence electron states have been calculated, taking into account the results from core level spectroscopy indicating the co-presence of two possible configurations for adsorbed alaninol molecules.[26]

The electronic molecular states found on the lower and higher BE side of the main 3d copper electronic states were identified, respectively, as due to antibonding state (peak A) and bonding state (buried in peak B), originating mainly from the interaction of the Cu 3d states with the N 2p lone pair state of the alaninol molecule.[26] Localized electronic states outside d-band orbitals of transition metals are known to be formed when a strong interaction occurs between adsorbate and nearest-neighbor substrate atoms; 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.[30,31] In the BE range from 5 to 11 eV, further structures are found (B to D) which are associated with molecular orbitals that are spread over the entire molecule mainly arising from concomitant contributions of C 2p, N and O 2p orbitals. Peaks at binding energies higher than 13 eV, labeled E and F in Figure 1b,

originate mainly from C 2s, N 2s, and O 2s electrons. The angular 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 $\bar{\Gamma}-\bar{X}$, $\bar{\Gamma}-\bar{M}$ lines and 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 PE spectra for 1 ML of L- (panel c) and D- (panel b) enantiomers of alaninol adsorbed on Cu(100) taken at normal emission with 30 eV photon energy using right (red solid line, RCP) and left (black solid line, LCP) circularly polarized light. The difference between the photoelectron intensities obtained with right and left circular polarized light for L- and D-alaninol, i.e. the dichroic spectrum, is reported in Figure 2a as blue and red solid line, respectively, and shows features in close correspondence with the previously outlined valence PE structures. LEED patterns, reported in the insets of Figure 2b and 2c, show (4 -1, 1 4) or (4 1, -1 4) molecular superstructures rotated clockwise or counterclockwise by 14° with respect to the [011] Cu direction for D- and L-alaninol respectively (red circles indicate copper diffraction spots).[23-25]

The reported difference spectra, measured on two samples prepared exposing the Cu(100) surface, separately, to the L- and D-alaninol, present a mirror image behavior. This result clearly proves that these dichroic signals originate only from the chiral nature of the alaninol-copper system and wipes out any doubt on the correctness of the used experimental configuration and on the possibility of spurious chiral effects from experimental geometry.[18] The invariance of the experiment for the application of the parity operation, that changes the handedness of the molecule and helicity of the photons, is demonstrated allowing us to discriminate and characterize the chiral properties of the valence electronic states of this system. Values of the $A_{CDAD}$ of 0.15±0.01, 0.05±0.01, 0.08±0.01, -0.05±0.01 were found (at hν=30 eV) for the peaks labeled A to D, respectively. Values close to zero for $A_{CDAD}$ have been obtained for peaks E and F. Only few of the valence band orbitals present dichroic effects at 30 eV photon energy. A negligible $A_{CDAD}$ value is obtained in the Cu 3d BE range (2 - 4 eV), indicating that electronic states ascribed to copper not involved in the adsorption mechanism do not present any chiral character.

Assignment of valence electronic states in the PE spectrum could be difficult because of the overlapping due to their close BE positions. The shape of the dichroic spectrum allows better definition of the contributions from molecule-Cu interactions to the valence photoelectron features, in energy regions where their overlapping does not permit sufficient energy discrimination. In fact, Figure 2a permits us to assign the peaks from B to E to different electronic states because their dichroic signals are different in intensity and shape. Dichroism is clearly recognized in the high BE side of feature D putting in evidence the contribution of a molecular state to the VB; moreover, this

feature shows opposite sign in the dichroic behavior with respect to the others. The difference in sign indicates that peaks B and C can be considered as the sum of electronic states with different symmetries. The shape of bands B and C is broad and bell-shaped (Figure 2a) not allowing specific identification. The effect of disentangling is particularly useful for peak A because it is buried below the tail of Cu 3d states and no clear information concerning full width at half maximum (FWHM) and peak shape can be derived from the direct analysis of the VB spectrum; on the contrary in the difference spectrum a narrow peak (240 meV of FWHM) is observed. The narrow FWHM value for peak A is comparable with what 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), corresponding to an intrinsic bandwidth of about 150 meV.[32] 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 transfer properties across the molecular-substrate interface. Therefore, precious information can be derived on the uniformity of the overlayer structure, the lifetime broadening, the vibrational coupling and the polarization/relaxation related phenomena.[32,33] The small bandwidth value of the peak A reflects the high degree of localization of the orbital and a long lifetime for the HOMO hole.

Dynamic effect on the $A_{CDAD}$ dichroic parameters in the VB spectrum has been studied as a function of photoelectrons kinetic energy at normal emission (varying the photon energy) and of the photoelectrons emission angle (at fixed photon energy). Figure 3 shows the dispersion of $A_{CDAD}$ values in the 25 eV to 42 eV photon energies range and -4° to 34° electron emission angles. As a function of the photon energy, a clear dynamic effect can be seen in the measured $A_{CDAD}$ parameters for the peaks A to D. In this photon energy range no dichroic effect is measured for peaks E and F at normal emission. As a general trend, we observe smooth changes in the $A_{CDAD}$ values as a function of the photon energy. Dynamic effects of valence states in CDAD photoelectron spectroscopy have been recently studied for alaninol in gas phase from experimental and theoretical point of view.[34] The average magnitude of $A_{CDAD}$ parameters founded for alaninol adsorbed on Cu(100) is higher than those measured for free alaninol[34] and for molecules adsorbed on surface in the cases of alanine on Cu(110) and 2,3-butanediol on Si(100) for C 1s core level.[20-22]

We studied the effect of the angular dependence on the dichroic parameters in the scattering plane defined by the [011] surface direction and the surface normal (see inset of Figure 1a). Modifications of the $A_{CDAD}$ parameters for peaks A to E as a function of the polar electron emission angle, θ, are shown in Figure 3b for 30 eV photon energy (peak F shows no dichroic signal). The

peak A shows a maximum of $A_{CDAD}$ at normal emission and decreases monotonically reaching zero at 10°; it remains zero at higher polar angles. A reversion in the sign in the dichroic parameter from positive to negative is observed for peak B at about 5°. Peak C presents smooth changes and reaches zero at 34° and peak D is always negative and presents no significant changes from -4° to 34°, in comparison with the other peaks. Peak E presents dichroism equal to zero around 0° and negative values for angles higher than 5°.

The above presented data show that CDAD measurements may reach values up to 15% for valence molecular orbitals and allow disentangle among electronic levels presenting different dichroic nature. Different structures of the $A_{CDAD}$ parameters associated to the different electronic orbitals in the valence band as a function of the photon energy and photoelectrons emission angle have been observed showing the high sensitivity of the $A_{CDAD}$ parameter to highlight the chiral features of a self-assembled 2D structure. The $A_{CDAD}$ parameter is also sensible to the chiral behavior of the valence electronic states depending on the character of the initial states; states with a predominant π character (A to D) present larger mean amplitudes of the dichroic signals when compared with states with predominant σ character (E and F).

We obtain direct information on the chirality transfer from chiral adsorbed molecule to the surface. This effect is expected to be observed in the core levels photoemission of the substrate atoms, but it is very weak because only a small portion of the photoemission signal originates from atoms that are influenced by the presence of the molecules.[22] The reported CDAD measurement performed on the valence band increase surface/interface sensitivity allowing to identify the dichroism of the newly formed antibonding peak A and to demonstrate that adsorption of chiral molecules on achiral surfaces produces a sharing of chirality between the molecule and the surface atoms underneath. We also pointed out that peak A, taking into account its dynamic effect as a function of the photon energy and emission angle, is more localized around the surface normal direction and shows higher mean values of $A_{CDAD}$ when compared with the other valence orbitals. The dynamic behavior can be associated to the attribution of peak A to mixed antibonding alaninol-copper orbital.

To get a deeper insight in the chiral properties of alaninol/Cu(100) interface we should consider that the sign and the magnitude of the circular dichroism in a CDAD experiment is related to the irreducible representation of the point group of the overall adsorption system (chiral molecule and copper atoms) in the electronic transition from initial valence band into continuum final states; the effect is proportional to the interference of dipole matrix element pairs.[11,12] At present, major theoretical efforts have been directed towards the dichroic study of gas phase chiral molecules and good agreement with experimental results has been obtained.[14] It has been theoretically shown that

molecular geometry is very important to obtain correct $A_{CDAD}$ parameters; slight difference in the conformer distribution, in the vibrational content or in rotation of a molecule portion (e.g. $CH_3$) produces significant changes in the sign and/or magnitude of the circular dichroism.[34-36]

In conclusion, we have investigated, by using circular dichroism in the angle distribution of valence photoelectrons, the chiral electronic features of the extended 2D domain of chiral self-assembled molecular structure originating from the adsorption of L- and D- alaninol on Cu(100). $A_{CDAD}$ parameters, which are related to the chirality of each valence molecular orbital, have been measured and it has been found that its magnitude depends on photon energy and electron emission angle (up to 15%) and on the predominant character of the initial electronic states ($\pi$ or $\sigma$). $A_{CDAD}$ is shown to be a sensitive tool to disentangle the small localized chiral electron contribution into the overlapping valence band largely representative of the achiral electronic states of the substrate. A direct information on the chirality transfer from the chiral adsorbed molecules to the underneath atoms of the achiral surface has been obtained through the analysis of the dichroic signal originating from the newly antibonding alaninol-copper orbital formed in the chemisorption process; on the contrary, non-interacting copper atoms do not present any dichroic signal. Although theoretical calculations are highly desirable for deeper insight and we hope that our results will motivate them, we believe that the study of the CDAD dichroic 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 to control the functionality of the molecule/surface interfaces.

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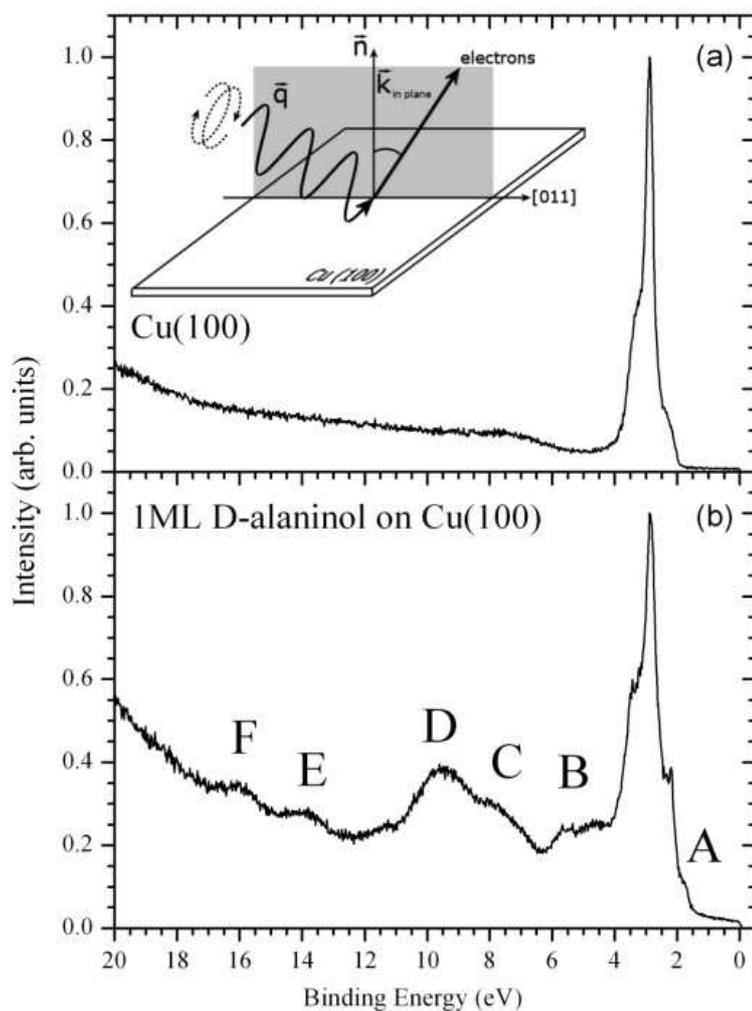
**Figure 1.** Photoelectron valence band spectra (sum over LCP and RCP light) obtained at normal emission (hν=30 eV) for clean Cu(100) (a) and 1 ML of D-alaninol adsorbed on Cu(100) at RT (b). Labels A to F indicate peaks attributed to alaninol. The inset in panel a shows a schematic sketch of the experimental geometry (**k** and **q** are the directions of the photoelectrons and of the incident light respectively and **n** is the surface normal).
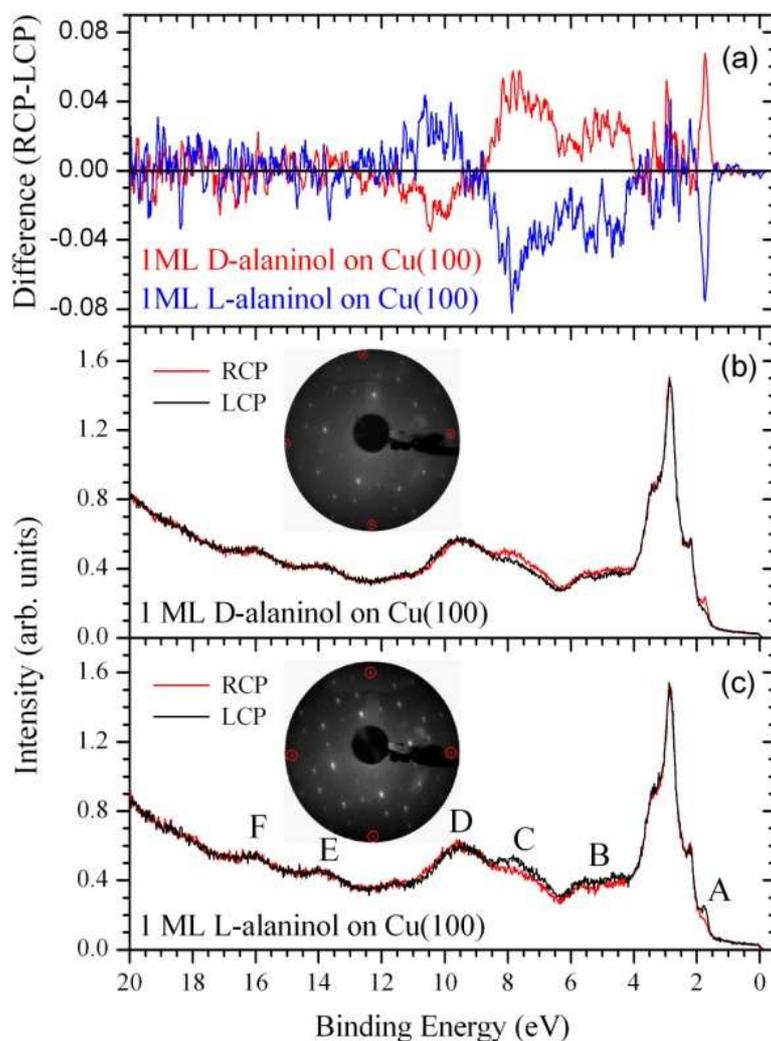
**Figure 2.** Circular dichroism in the valence photoelectron spectra for alaninol adsorbed on Cu(100) (RT, normal emission, hν=30 eV). Valence photoelectron spectra for D- and L-alaninol obtained with right (red solid line, RCP) and left (black solid line, LCP) circular polarized light are reported in panels (b) and (c) respectively. Difference (RCP-LCP) for L- and D-alaninol are reported in panel (a) as a blue and red solid line respectively. The insets show the LEED patterns of 1 ML of D- (b) and L- (c) alaninol; red circles indicate the diffraction spots due to copper.
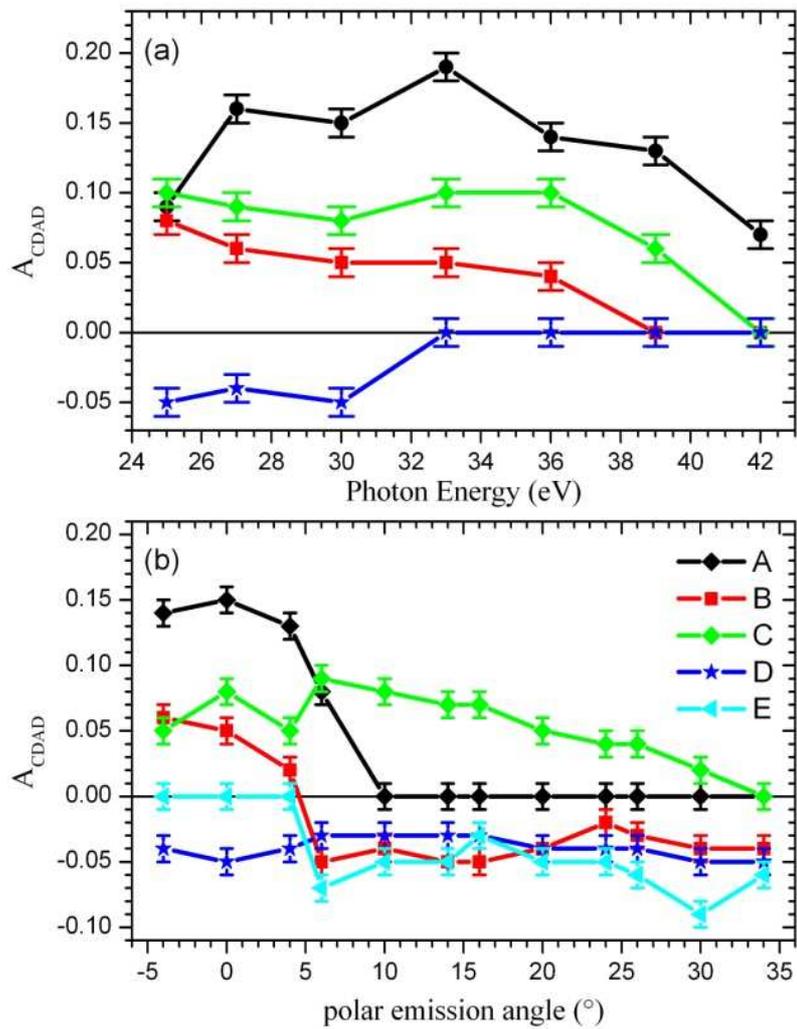
**Figure 3.** Circular dichroism ($A_{CDAD}$) in the photoelectron valence spectra for 1 ML of alaninol adsorbed on Cu(100) at RT measured in the scattering plane defined by the [011] surface direction and the surface normal (see inset of Figure 1a). $A_{CDAD}$ for valence structures labeled in Figures 1 and 2 measured as a function of the photon energy in normal emission (a) and of the polar electron emission angle at 30 eV of photon energy (b) (note that valence structures E and F present zero $A_{CDAD}$ when not reported).