

Can circular dichroism in core-level photoemission provide a spectral fingerprint of adsorbed chiral molecules?

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Abstract. The results of experimental measurements and theoretical simulations of circular dichroism in the angular distribution (CDAD) of photoemission from atomic core levels of each of the enantiomers of a chiral molecule, alanine, adsorbed on Cu(1 1 0) are presented. Measurements in, and out of, substrate mirror planes allow one to distinguish the CDAD due to the chirality of the sample from that due to a chiral experimental geometry. For these studies of oriented chiral molecules, the CDAD is seen not only in photoemission from the molecular chiral centre, but also from other atoms which have chiral geometries as a result of the adsorption. The magnitude of the CDAD due to the sample chirality differs for different adsorption phases of alanine, and for different emission angles and energies, but is generally small compared with CDAD out of the substrate mirror planes which is largely unrelated to the molecular chirality. While similar measurements of other molecules may reveal larger CDAD due to molecular chirality, the fact that the results for one chiral molecule show weak effects means that such CDAD is unlikely to provide a simple and routine general spectral fingerprint of adsorbed molecular chirality.

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1. Introduction

While photoemission is intrinsically a probe of the electronic structure, core-level photoemission in the form of x-ray photoelectron spectroscopy (XPS) is a routine technique for the determination of surface composition, exploiting the fact that core-level binding energies are characteristic of the elemental species [1]. Nevertheless, subtle shifts in the photoelectron binding energy of these core levels are also exploited in XPS to provide a spectral fingerprint of the ‘chemical state’ of the near-surface atoms as well as their elemental identity [1]. In addition, measurements of the variation in the core-level photoemission intensity as a function of emission angle or photoelectron energy (through variation of the photon energy) provide local structural information through the phenomenon of photoelectron diffraction, which exploits the coherent interference of the directly emitted photoelectron wavefield with components of the same wavefield elastically scattered by surrounding atoms [2]. Here, we present new results which address the question of whether a simple variation of this photoelectron diffraction method can provide a spectral fingerprint of the chirality of the structural environment of surface atoms within a molecular adsorbate.

There has been growing interest in the last few years in the properties of chiral molecules adsorbed on surfaces e.g. [3]–[8], motivated in part by the potential practical importance of enantioselective heterogeneous catalysts: i.e. the ability to generate molecular products of a single chiral enantiomer (of a single ‘handedness’) by a surface reaction. In such studies it is clearly straightforward to know the chirality of any molecules exposed to the surface or removed from the surface as products of a reaction using standard chemical methods, but it is less simple to establish whether molecular species adsorbed on the surface (which may be reaction intermediates) are predominantly of a single chirality or are simply a racemic mixture (i.e. contain both enantiomers in equal amounts). A simple spectroscopic means of establishing this would be of great value.

An important general property of chiral molecules is that they display circular dichroism in optical absorption, i.e. the absorption is different for circularly polarized light of opposite senses. Notice that there is some ambiguity in the way that circular dichroism is defined; here we take it to be the normalized difference in the signals being measured with radiation of right- (I_+) and left- (I_-) handed helicity, i.e. as $(I_+ - I_-)/(I_+ + I_-)$. While this definition is a natural one in describing undulator radiation, it is common in optics to describe light of right-handed helicity as left-circularly polarized; the difference arises because it depends on whether one views the rotation of the E -vector of the radiation from behind or in front of the radiation travel (e.g. [9]). Unfortunately, there certainly appear to be instances in the literature in which references to

'right-circularly polarized radiation' actually mean right-handed helicity. Following a convention in circular dichroism in the angular distribution (CDAD) used previously [10], here we use $\sigma+$ circular polarization to mean right-handed helicity (and thus left-circularly polarized light) and $\sigma-$ to mean left-handed helicity (and thus right-circularly polarized light). Conventional optical absorption measurements of circular dichroism on sub-monolayer coverages of adsorbed molecules are likely to be very demanding and may not provide spectroscopically specific information regarding the adsorbed species. However, it has been suggested that spatially oriented chiral molecules, such as those adsorbed on a surface, should show CDAD of photoelectrons emitted from these species [11]–[13]. Indeed, such an effect has even been predicted for chiral molecules in the gas phase, in which they are randomly oriented [14], and a small effect (up to 5%) of this kind has recently been observed experimentally in both core level [15] and valence state [10, 16, 17] photoemission. One might therefore anticipate that this effect would be practically viable as a spectral fingerprint of adsorbed (oriented) chiral species. Of special interest would be CDAD in photoemission from core levels, as the elemental and chemical-state specificity offered by photoelectron binding energies would allow one to localize the chirality information to specific adsorbed species on a surface.

This simple prediction is complicated, however, by the fact that when a molecule is adsorbed on a surface the geometry of the CDAD experiment must be chosen with great care if one is not to observe effects which are wholly unrelated to the chirality of the adsorbate. In particular, if the plane defined by the incident (circularly polarized) light and the photoelectron collection direction, does not correspond to a mirror symmetry plane of the sample, the experiments conducted with opposite circular polarizations will not be equivalent and so a circular dichroism signal will be observed. An early review of CDAD studies of surfaces which are not chiral discusses these symmetry requirements further [18]. The CDAD effect from core levels of atoms at non-chiral surfaces is now well-established, and there have been many demonstrations of substantial CDAD signals of 50% or more from highly symmetry crystal surfaces (e.g. Si(1 0 0) [19, 20] and W(1 1 0) [21]), from adsorbed atoms (e.g. Rb and K [22]) and from adsorbed linear molecules (notably CO [23]–[25] and NO [26]); we stress that none of these samples are themselves chiral, but the geometry of the experiments in which the CDAD was observed was chiral. All of these experiments involved measurements of the angular dependence of the photoemission at fixed photon energies, but utilized two rather different geometries. In the case of the adsorbate systems cited above, the photoemission intensities (and circular dichroism) were measured as a function of the polar emission angle (relative to the surface normal) in a plane perpendicular to that defined by the incident photons and the sample surface normal. In these experiments the CDAD is expected to vanish at normal emission, providing the incident plane corresponds to a mirror plane of the substrate, and indeed this was found to be the case. In the studies of core-level photoemission from substrate atoms, the azimuthal angular dependence of the emission was measured at fixed polar angles, the sample being rotated about its surface normal with the photons incident along the surface normal. In these experiments the CDAD signal vanished when the azimuth of electron emission corresponded to a mirror plane of the substrate. An interesting feature of the results of these experiments is that the main difference between the azimuthal emission patterns measured with unpolarized radiation and with left- and right-circularly polarized radiation is an azimuthal rotation. With unpolarized light, the pattern reflects the full point group symmetry of the substrate, but with circularly polarized light the pattern was rotated a few degrees clockwise or counter-clockwise such that the rotational symmetry of the substrate was retained but the mirror symmetry was lost. Evidently the difference between the

emission measured from the two different circular polarizations due to these opposite rotations of the emission pattern vanishes in the mirror planes of the substrate.

The fact that such large CDAD signals can result from non-chiral structures clearly raises an important question for the viability of CDAD as a useful spectral fingerprint of adsorbed chiral molecules: namely, is the effect being sought sufficiently large to overcome residual signals caused by imperfections in the experimental geometry used? It is this question which we address in this paper with a series of experimental and computational studies of model systems [27]. In particular, we have made measurements of CDAD of core-level photoemission from alanine on Cu(1 1 0). Alanine, $\text{NH}_2\text{CH}_3\text{C}^*\text{HCOOH}$, is the simplest chiral amino acid having a chiral centre at the C^* atoms (the so-called $\alpha\text{-C}$) which is bonded to a NH_2 amino, CH_3 methyl, atomic H and COOH carboxylic acid group. On adsorption on Cu(1 1 0), the acid hydrogen atom is lost to form what is strictly alaninate, $\text{NH}_2\text{CH}_3\text{C}^*\text{HCOO}^-$, although for convenience the resulting adsorption phases are commonly referred to as being of alanine. This adsorption system displays two different ordered phases. Adsorption at room temperature followed by annealing to about 420 K, or adsorption at this surface temperature, leads to the formation of a complex-ordered phase described by the matrix $\begin{pmatrix} 2 & -2 \\ 5 & 3 \end{pmatrix}$ or the matrix $\begin{pmatrix} 5 & -3 \\ 2 & 2 \end{pmatrix}$ depending on which enantiomer of alanine is used, whereas further heating to about 470 K leads to the formation of a nominal (3×2) ordered phase [6]–[8, 28]. On the basis of STM and vibrational spectroscopy, the lower-temperature phase has been attributed to the presence of two differently oriented alaninate species within the unit mesh, one probably bonded to the surface through both the carboxylate O atoms and the amino N, the other bonded only through one of the carboxylate O atoms. The long-range ordering of this complex phase is itself chiral, as indicated by the different matrix notation for the two distinct enantiomers, i.e. the diffraction pattern lacks the mirror symmetry plane of the substrate, and the diffraction patterns of the equivalent phases formed by the two enantiomers of alanine are related by a mirror-reflection operation.

In the (3×2) phase, only a single alaninate species is thought to be present, bonded to the surface through both O atoms and the N; for this phase, the analogy with adsorption of the simpler (non-chiral) amino acid glycine ($\text{NH}_2\text{CH}_2\text{COOH}$), provides a firmer basis for this structural assignment. In particular, glycine has been studied extensively on Cu(1 1 0) [29]–[34]; this molecule also deprotonates on adsorption and forms a (3×2) ordered phase. In this phase the local geometry of the bonding atoms, with the N atoms essentially atop surface Cu atoms and the two O atoms off-atop other surface layer Cu atoms, has been established quantitatively by scanned-energy mode photoelectron diffraction (PhD) [32, 33], the structure agreeing well with the results of density functional theory (DFT) calculations [31, 34]. It appears from STM images [8], recent theoretical total-energy calculations [35], and a new PhD study, that the local bonding geometry of alanine on Cu(1 1 0) is similar to that of glycine [36]. Figure 1 shows a schematic diagram of the local structures of glycinate and alaninate on Cu(1 1 0), in each case as obtained from theoretical calculations [34, 35] (subtle substrate distortions have been omitted for simplicity). Notice that, while glycine is not chiral in the gas phase, adsorption on the surface does create a chiral species because, relative to the geometry shown in figure 1, the N atom must either appear to the left or the right of the C–C backbone, and these two conformations are mirror images of each other. However, because the molecule is not chiral in the gas phase and the surface has a mirror plane along $\langle 1\ 0\ 0 \rangle$ (essentially the direction of the C–C backbone), the surface glycinate must comprise a racemic mixture with no net chirality; whether this comprises heterochiral domains or homochiral domains [37] does not influence this conclusion.

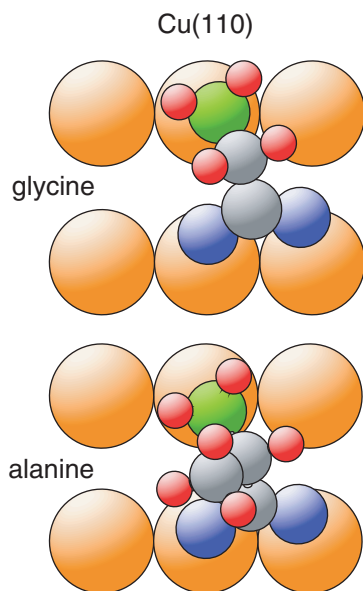


Figure 1. Schematic diagram of the adsorption geometries of glycine and alanine on Cu(1 1 0). The diagrams are based on the results of theoretical total energy calculations [34, 35] but do not include subtle distortions induced in the substrate.

In considering the proper geometry to search for chirally generated CDAD, it is important to recognize that the complete surface produced by adsorbed alanine is chiral—i.e. the adsorbed chiral molecule destroys the mirror symmetry of the substrate. This must be true even for the (3×2) phase in which the long-range ordering is not itself chiral, and thus the diffraction pattern (i.e. the relative locations of the diffracted beams) does not appear chiral. Notice, in particular, that it is not only the environment of the α -C in the adsorbed alanine which is chiral—all the atoms in the molecule, and indeed even the substrate atoms, now have a chiral geometry. The loss of the mirror plane would, of course, also be true for any low symmetry adsorbate which is not chiral, such as a linear molecule which is tilted in some low symmetry azimuth. In this case, however, mirror image domains of the low symmetry local structure would co-exist with equal probability, and the spatial average of a spectroscopic measurement would thus retain the mirror symmetry of the substrate. By contrast, with a chiral adsorbate, no mirror image domain is possible if only one enantiomer of the molecule is adsorbed. Of course, the chirality of the complete surface arises from the adsorbed chiral molecule, and this complete chirality is thus a manifestation of the effect we are seeking to monitor. If we therefore make a CDAD measurement in a mirror plane of the underlying substrate we should see no effect if the adsorbate is not chiral (or comprises a racemic mixture) but should observe CDAD if a single enantiomer (or a significant excess of a single enantiomer) of the chiral species is present. It is this effect which we aim to observe and, as implied above, the effect may be expected to be seen in photoemission from any of the constituent atoms of the adsorbed molecule. Indeed, in principle it could also be seen in photoemission from the substrate atoms, although we may anticipate that this effect is probably very weak, because only a small proportion of the substrate photoemission signal comes from atoms sufficiently close to the adsorbed molecules to be influenced by their presence. This brings us to one of the key questions which we wish to address: how large is the chirally induced CDAD effect in an adsorbed chiral molecule? The symmetry arguments tell us that the CDAD in the

substrate mirror plane should not be identically zero with an adsorbed chiral molecule, but tell us nothing about how large the effect should be.

To answer this question we have undertaken a series of experimental measurements of the Cu(1 1 0)/alanine model system. These experiments are, however, quite time-demanding, because one is seeking to determine subtle differences between measurements with the two different forms of circular polarization, and there are many possible experimental parameters, such as the polar emission angle and the photoelectron energy, which can be varied. We have therefore also made some use of theoretical calculations which are relatively straightforward to perform and give further information on the size of the effect under different measurement conditions. Early theoretical work on the CDAD phenomenon focused on dichroic effects associated with interference in non-dipole photoemission excitation [11]. However, it is now recognized that CDAD can be readily accounted for by assuming only simple dipole excitation [13]; the effect arises from the same final-state electron elastic scattering phenomena which are exploited in photoelectron diffraction. CDAD can therefore be modelled by standard multiple scattering photoelectron diffraction codes, requiring only minor modifications to include the effects of the circular polarization (see, e.g. [20, 21, 25]) on the dipole matrix element. Spin-resolved phase shifts are not needed, as only photoemission from 1s states has been measured. In the present case, we used a slightly modified version of the codes developed by Fritzsche [38]–[40], which we have used extensively and successfully to simulate PhD data, in order to determine a wide range of adsorbate surface structures (e.g. [2]). We stress that our primary objective in performing these calculations for adsorbed alanine and glycine is not to fit our experimental data; these theoretical results are sensitive to the internal conformation of the adsorbed molecule and this is not known from previous work. However, such calculations provide an alternative way to evaluate the relative importance of CDAD due to the chiral surface, and CDAD due to a chiral experimental geometry, over a range of experimental parameters, and free from experimental noise.

2. Experimental and theoretical details

The experiments were conducted in a conventional ultra-high vacuum surface science end-station equipped with the usual facilities for sample cleaning, heating and cooling. In the several experimental runs which contributed data to this report, this end-station was installed on one of the UE56/2-PGM beamlines of BESSY II which comprise a 56 mm period undulator set to deliver circularly polarized radiation, followed by a plane grating monochromator [41]. Notice that at the photon energy of 310 eV chosen for many of our measurements of C 1s photoemission some contamination of the beamline optics leads to imperfect (82–95%) circular polarization of the final beam [42]; as our data analysis assumes 100% circular polarization this means our CDAD measurements of C 1s emission underestimate the dichroism by about 10–20%. Different electron emission directions can be detected by rotating the sample about its surface normal (to change the azimuthal angle) and about a vertical axis (to change the polar angle). Sample characterization *in situ* was achieved by LEED and by soft-x-ray photoelectron spectroscopy (SXPS) using the incident synchrotron radiation. These wide-scan SXPS spectra, and the narrow-scan C, N and O 1s spectra used in the CDAD measurements, were obtained using an Omicron EA-125HR 125 mm mean radius hemispherical electrostatic analyser equipped with seven-channeltron parallel detection which was mounted at a fixed angle of 60° to the incident x-radiation in the same horizontal plane as that of the polarization vector of the radiation.

The Cu(1 1 0) crystal was cleaned *in situ* by Ar ion bombardment followed by brief annealing. The L-alanine and D-alanine powders were contained in glass tubes which could be heated via surrounding copper coils, the temperature being measured by a thermocouple attached to a wire mesh within the tube. A similar doser was charged with glycine powder for some comparative studies. The dosers were held within small, separately pumped side-arms separated from the upper chamber by a gate valve. Each source was outgassed for several hours prior to initial use. During dosing of alanine the source tube was heated to about 370 K and the Cu(1 1 0) crystal, either at 400–430 K or at room temperature, was positioned facing the open gate valve to the doser. It was found that to achieve a saturated overlayer, as judged by monitoring the heights of the N 1s, O 1s and C 1s photoemission peaks, the crystal had to be exposed to the alanine flux for 30 min. The pressure in the preparation chamber rose from a base pressure of 1×10^{-10} mbar to around 1×10^{-9} mbar during dosing. Sharp overlayer LEED patterns of both overlayer phases (complex and (3×2)) were seen at successively higher annealing temperatures, but because of the susceptibility to electron beam damage, LEED was not normally used prior to the CDAD measurements once a reliable preparation recipe had been established. In the case of glycine deposition a (3×2) adsorbate phase was formed during deposition onto the surface at room temperature, but if dosing of alanine was conducted with the sample at room temperature then annealing to about 430 K was required to order the complex phase, while further heating to 470 K produced the (3×2) phase.

The core measurements used to extract the CDAD were short range (30 eV) photoelectron energy spectra around the core-level photoemission peaks of interest (C 1s, N 1s and O 1s from the alanine and Cu 3s as a reference of the substrate emission) using the two opposite circular polarizations of the incident photons. From these measurements the area of the photoemission peaks could be extracted by simple curve fitting to the peak(s) and background. The UE56/2-PGM beamlines are fitted with two canted variable-polarization undulators, so CDAD measurements could be taken either by switching the polarization of a single undulator or setting the two undulators to deliver light of opposite circular polarization, then switching the measurements between the two sources. In principle, this latter mode of operation is much more convenient, but in practice we experienced considerable problems in obtaining reliable dichroism data in this way, possibly due to problems in proper referencing of the incident beam flux, I_0 , but also possibly due to differences in the positions of the two monochromatic beams on the sample (and thus different positions relative to the electron energy analyser). All the CDAD measurements reported here were therefore obtained by sequential measurements of the photoemission spectra with left- and right-circularly polarized light obtained by adjusting a single undulator. Even in this case, the method of proper normalization of the two measurements of opposite polarization proved a source of concern. The main normalization was based on the drain current of the final post-focusing mirror in the beamline, but in some measurements comparison of the results for the two polarizations after this normalization revealed differences in the background levels under the peaks which suggested that the normalization was not correct. Of course, in the inelastically scattered background close to the low kinetic energy side of an adsorbate photoemission peak, we may expect some residual intrinsic dichroism arising from the chirality. In general, however, the substrate emission, which is the main source of the inelastic background, is unlikely to show significant chirality. Alternative normalization schemes based on the inelastically scattered background signal at kinetic energies higher than that of the peak being measured were therefore also tested as a means of normalization. In the CDAD measurements presented here, the estimated precision includes the scatter of these different

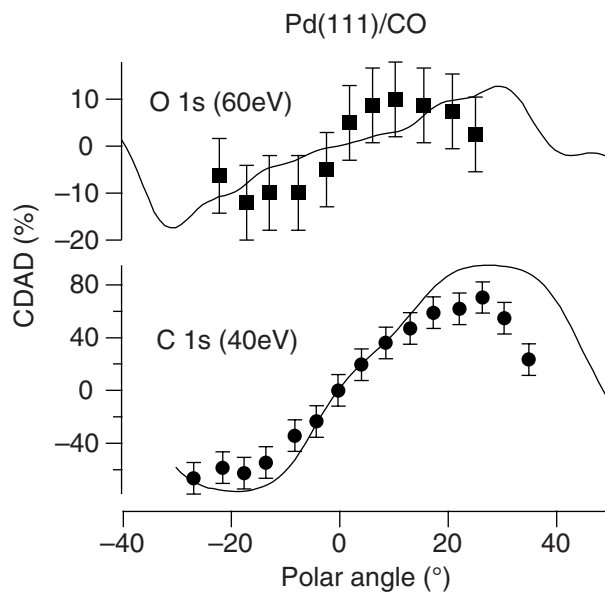


Figure 2. Comparison of the results of our theoretical calculations (lines) and (corrected) experimental measurements [23, 24] for CDAD from C and O 1s photoemission at relatively low kinetic energies from CO adsorbed on Pd(1 1 1). Measurements were made as a function of polar emission angle in the plane perpendicular to that defined by the incident photon direction and the surface normal. The C–O axis is perpendicular to the surface so the structure is non-chiral, but the experimental geometry is chiral except in the case of emission along the surface normal.

normalization methods. Data sets for which different methods of normalization led to large variations in the implied CDAD were rejected as unreliable. Note that carbon contamination of the monochromator optics is known to influence the degree of circular polarization of the excitation x-ray radiation in the energy range of strong absorption, but all measurements reported here are for photon energies above this range.

Theoretical simulations were performed using the computer programs developed by Fritzsche [38]–[40] for the description of photoelectron diffraction in the lower energy range (typically less than about 500 eV), typically used when exploiting backscattering. These programmes describe the final state elastic scattering which gives rise to CDAD in core-level photoemission and required only minor modification to include circularly polarized incident radiation. As a test of these modifications, we first ran simulations of published experimental data of Bansmann *et al* [24] on a non-chiral adsorbate system, notably CO adsorbed on Pd(1 1 1). This is an adsorption system for which we have previously determined the local adsorption structure by photoelectron diffraction [43]; in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase studied in the CDAD experiments, the CO molecules occupy the ‘fcc’ hollow sites directly above third layer Pd atoms. Figure 2 shows a comparison of the experimental data and the theoretical simulations for measurements of the dependence on the polar emission angle of the CDAD from C 1s and O 1s at relatively low kinetic energies. In these experiments the detector was scanned in a plane perpendicular to the surface and perpendicular to the plane defined by the surface normal and the incident circularly polarized radiation. There is some ambiguity in the experimental publication regarding

the azimuthal plane, but our calculations show very similar results for the two inequivalent high-symmetry azimuths of this surface. Figure 2 shows clearly that our calculations reproduce the experimental results well both in terms of the angular dependence and the amplitude of the CDAD. (Note that figure 2 shows the corrected experimental amplitudes of the later paper by Bansmann *et al* [24]; the original publication of these data [23] showed weaker CDAD due to an incorrect assumption regarding the degree of circular polarization of the incident radiation.) Our calculations also revealed very little influence of the presence (and hence location) of the Pd(1 1 1) substrate, somewhat surprising at these low energies at which backscattering is strong; this effect has also been seen in other theoretical simulations of these C 1s data by Westphal *et al* [25]. Indeed, the much larger amplitude of CDAD for the C 1s emission relative to that for the O 1s emission is consistent with the implication that forward scattering (possible off the O atom for C 1s emission) contributes more strongly than backscattering (the only possible type of scattering from the O 1s emission). Notice, incidentally, that the CDAD in these experiments (and theory) is zero at normal emission, as required by symmetry for this non-chiral adsorbate.

3. Results

Based on the arguments presented in section 1 an experimental demonstration of the CDAD effect arising from adsorbate molecular chirality should be performed using photon incidence and electron detection in a mirror plane of the substrate for which no CDAD should be observed in the absence of this chirality. However, if the CDAD arising from the surface chirality is very small compared with that from a chiral experimental geometry, it is possible that CDAD in such a measurement might reflect only that the experimental geometry is not exactly in the substrate mirror plane. To avoid this hazard we have made measurements for fixed (coplanar) incidence and polar-emission angles as a function of the azimuthal angle of the surface, relative to the expected positions of the mirror planes. Such a measurement also provides a direct measure of how the CDAD varies with azimuthal angle in geometries close to the mirror planes, thus providing some indication of the scale of the problem in distinguishing CDAD arising from a chiral experimental geometry from the more interesting effect due to the molecular chirality. Notice that, somewhat counterintuitively, these measurements are potentially more reliable for non-normal emission than for normal emission, because a slight misorientation of the sample may cause a nominally normal emission measurement to be made for a small off-normal emission angle which is out of the incidence plane, thus giving rise to a chiral experimental geometry at all incident azimuths. Such an effect would be far less significant well away from normal emission. In our experiments, simultaneous measurements of the Cu 3s photoemission provided a check of the experimental geometry, because we anticipate that this signal will probably show essentially no CDAD in the substrate mirror planes. One further way of checking that any observed CDAD in the substrate mirror plane really is due to the molecular chirality, is to conduct the measurement with each of the two enantiomers of alanine; the true molecule-induced CDAD signals should be equal and opposite for these two measurements.

Figure 3 shows the results of such measurements from the (3×2) alaninate phase, using a photon energy of 310 eV and polar incidence and detection angles of 30° , for C 1s photoemission from the three chemically distinct C atoms. These lead to three chemically shifted C 1s photoemission peaks (figure 4) which can be separated by careful fitting to the three components. Note that while it is difficult to ensure that such a fitting procedure to a single spectrum gives

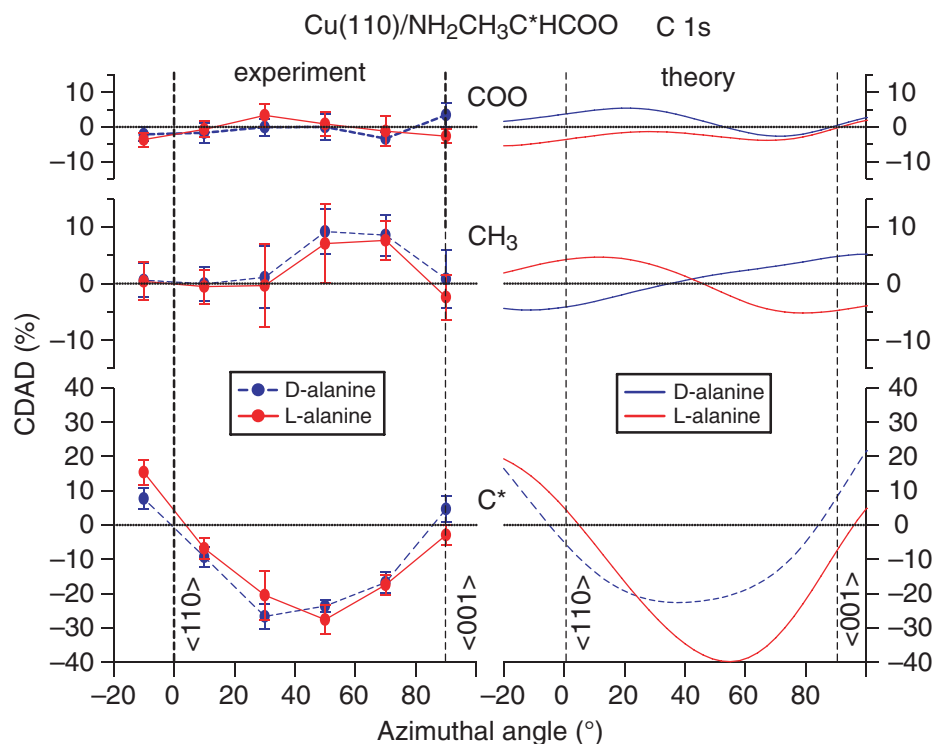


Figure 3. Experimental results for the azimuthal angle dependence of C 1s photoemission CDAD from the (3×2) phases of each enantiomer of alaninate on Cu(110), measured at a polar emission angle of 30° and a photon energy of 310 eV. The experimental results are shown on the left and the results of theoretical simulations on the right. Experimental error bars are obtained from scattering in the processed data arising from different normalization procedures.

a unique solution, our data comprise many spectra taken at different emission angles and with different polarizations. Fitting all of these spectra to the same three components with only the relative amplitudes of the three peaks varying is far more heavily constrained. The inset to figure 4 shows how the C 1s spectra change when switching between the two distinct circular polarizations in a geometry (out of a substrate mirror plane) in which the circular dichroism is particularly pronounced. Notice, incidentally, that the relative amplitudes of the three C 1s photoemission components depend quite strongly on the photoelectron-emission angle and energy due to photoelectron diffraction, and thus do not reflect the stoichiometry of the surface species. Also shown in figure 3 are the results of theoretical simulations based on a molecular orientation on the surface similar to that shown in figure 1; some limited optimization of the bond angles was made to improve the agreement, but this structural search was not exhaustive. The resulting theoretical simulations reproduce the largest CDAD effects seen in the experimental data, but certainly do not provide a full description of the more subtle variations.

Several significant effects are seen in the experimental data of figure 3. Firstly, away from the substrate mirror planes, the CDAD is significant for emission from both the methyl and α -C (C^*) carbon atoms, with a value up to about 25% in the latter case. However, this large CDAD signal is found experimentally (and theoretically) to be of the same sign for both enantiomers, clearly showing that this effect is due to the chiral experimental geometry in these azimuthal planes, and

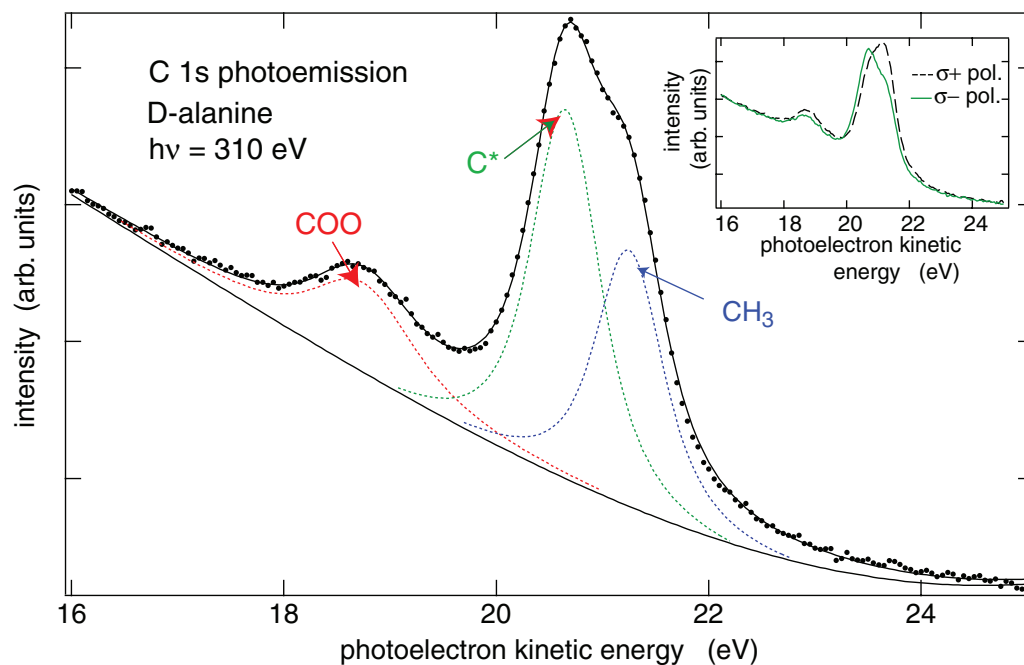


Figure 4. A representative C 1s photoemission spectrum as used in the CDAD measurements of figure 3 from adsorbed D-alanine in the (3×2) phase on Cu(110), showing the separation of the three distinct chemically shifted components. Note the absolute photoelectron kinetic energy scale is uncorrected for contact potential differences. The inset shows a pair of C 1s spectra from the same surface phase taken in $\sigma+$ and $\sigma-$ circular polarization in a geometry in which the dichroism is particularly clearly seen in these raw data (normal incidence, 60° polar emission angle, 10° azimuthal angle—see figure 5); note that this geometry is not in one of the substrate mirror planes.

not to the molecular chirality. In contrast, in the two substrate mirror planes, the CDAD is much weaker (typically 5% or less). However, in the $\langle 001 \rangle$ azimuth, at least, there is a residual effect which is of opposite sign and approximately equal magnitude for the two enantiomers. Moreover, for the COO and C emitters, at least, this effect appears to be statistically significant. The data of figure 3 thus demonstrate that CDAD entirely due to molecular chirality can be observed, and that the effect is not only at the chiral centre of the molecule—conclusions entirely consistent with expectations for a chiral molecule which is oriented in space. On the other hand, these results also show that, at least for this model system, the CDAD effect due to the molecular chirality is weak, and in particular, is significantly weaker than that which can arise from a chiral experimental geometry independent of the molecular chirality.

While most of our experiments focused on the (3×2) ordered phases for which the local adsorption geometry is thought to be moderately well understood, several measurements were made of both the (3×2) phase and the complex phase obtained without the higher temperature annealing. These data were recorded in a slightly different geometry, notably normal incidence (and hence 60° polar-emission angle, as defined by the fixed angle between the incident direction and the fixed electron energy analyser). Figure 5 shows CDAD results for the C 1s emission for both phases in this geometry. For the (3×2) phase the results are comparable to those of figure 3,

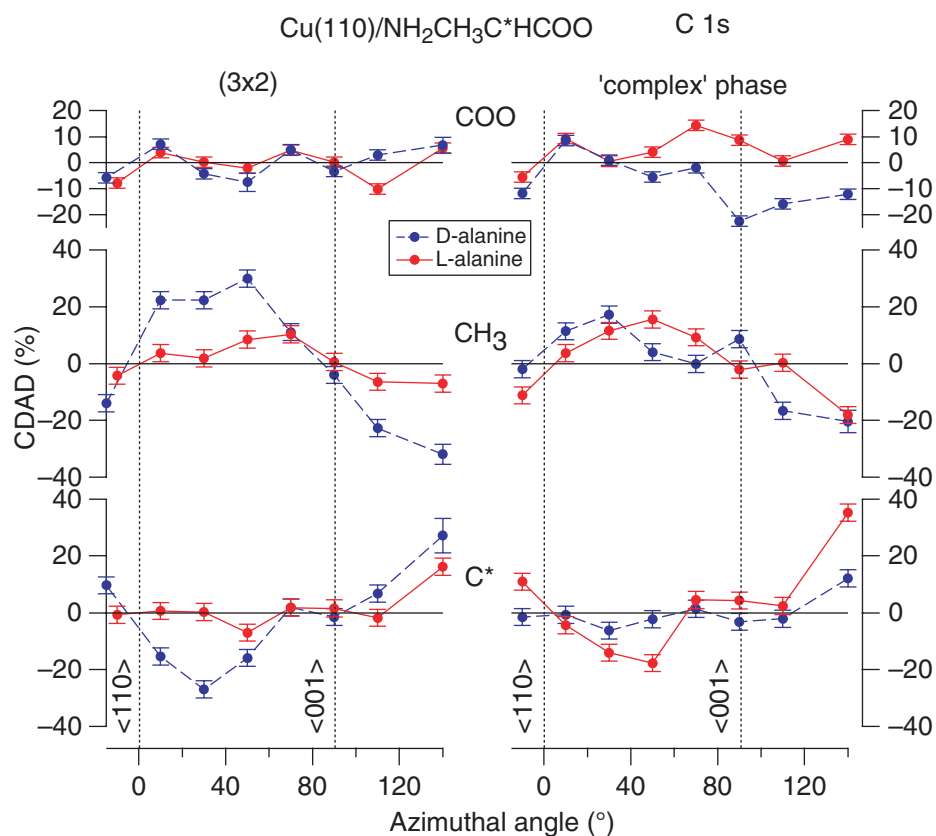


Figure 5. Azimuthal angle dependence of the C 1s photoemission CDAD from the two enantiomers of alanine adsorbed onto Cu(110) in the (3×2) and 'complex' ordered phases, measured at normal incidence, 60° polar-emission angle and a photon energy of 310 eV.

in that the CDAD is very weak for all three C emitters in the substrate mirror planes; in these mirror planes there is some indication of weak residual CDAD which switches sign between the two alanine enantiomers, but with reasonable allowance for the experimental errors these residual signals are less convincing than in figure 3 with a different emission geometry. For the complex phase, however, significantly larger CDAD signals are seen in the substrate mirror planes, and while in some cases (notably the carboxyl C emitter in the $\langle 001 \rangle$ azimuth) the magnitudes of the CDAD of the two enantiomers do differ somewhat, there is clear evidence for CDAD induced by the molecular chirality for all the C emitters in both substrate mirror planes. It is difficult to generalize reliably from the limited range of experimental parameters explored, but this trend for the complex phase to show stronger molecular chirality-induced CDAD than the (3×2) phase did appear to be consistent. In fact, it is possible that this effect contributed to our difficulty in obtaining reliable results for the (3×2) phase, as slight variations in the annealing condition may lead to a mixed phase not fully transformed to (3×2) . Notice that preparations of this phase after conducting the higher-temperature annealing were not checked with LEED prior to collecting the CDAD data, for fear of damaging the molecular layer with the electron beam; instead, the core-level photoemission was used as a spectral fingerprint of the state of the surface, established in initial characterization studies which included LEED observations. In many of the

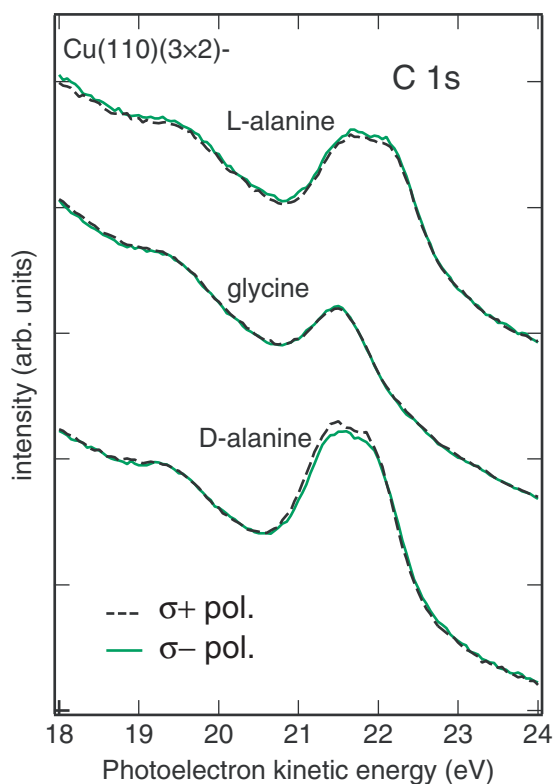


Figure 6. C 1s photoemission spectra from L-alanine, D-alanine and glycine in the (3×2) phase on Cu(1 1 1) recorded in right- and left-circularly polarized radiation measured in the $\langle 110 \rangle$ azimuth mirror plane of the substrate. The experimental geometry was normal incidence and 60° polar-emission angle and the photon energy was 310 eV.

CDAD experiments LEED patterns were also checked after collecting the photoemission data. Nevertheless, slight differences in the thermal treatment of the two enantiomers could have led to a loss of the anticipated equal-and-opposite CDAD in the substrate mirror planes.

While the opposite behaviour of the two enantiomers of the alanine provides a valuable demonstration that the residual CDAD in the substrate mirror planes does arise from the molecular chirality, a further test is provided by similar data for the (3×2) phase of glycine on Cu(1 1 0). As remarked earlier, glycine in the gas phase is not chiral, because while the C^* atom in alanine is bonded to a H atom and to the amino, carboxyl and methyl species, in glycine the methyl group is replaced by a second H atom. On the surface, on the other hand, the bonding through the two O atoms and the N atoms generates a chiral species (figure 1), but on average the surface must have an equal occupation of both enantiomers of this adsorption-induced chirality. In effect, the glycinate surface comprises a racemic mixture in which the CDAD from one enantiomer must cancel the CDAD from the other. Far less extensive experiments on glycine were performed, but figure 6 shows a set of C 1s photoemission spectra, recorded at normal incidence and 60° polar-emission angle in the $\langle 110 \rangle$ azimuth, from both alanine enantiomers and from glycine in $\sigma+$ and $\sigma-$ circular polarization. Notice, of course, that the spectra from glycine show only two inequivalent C atoms (the methyl C is missing). These spectra demonstrate not only the weak CDAD effect for the alanine, but also no detectable CDAD for the glycine, as expected.

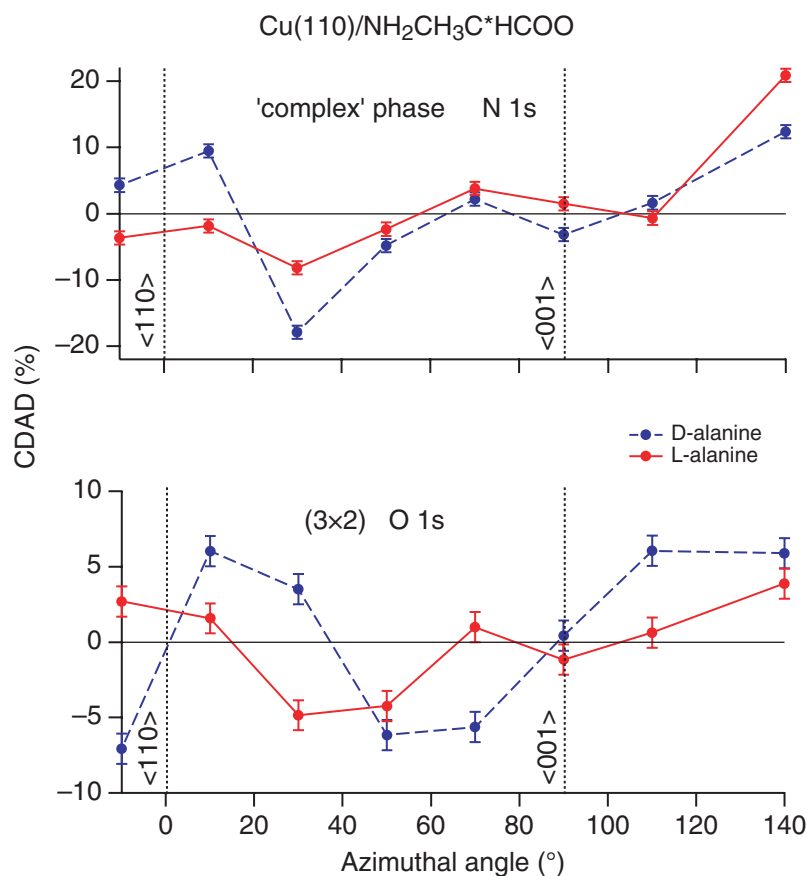


Figure 7. Azimuthal angle dependence of N 1s CDAD from the complex phase of both enantiomers of alanine on Cu(110) recorded at normal incidence, 60° polar-emission angle and a photon energy of 450 eV, together with similar data for O 1s emission from the (3 × 2) phase in the same geometry at a photon energy of 570 eV.

CDAD measurements were also made of the O 1s and N 1s photoemission, for both the (3 × 2) and complex alaninate phases and for other emission geometries and photon energies, but there was no experimental geometry for which a complete set of C 1s, O 1s and N 1s CDAD measurements of both enantiomers was judged to be reliable. For the N 1s, in particular, data for one enantiomer taken in the same geometry as the C 1s data of figure 3 do indicate meaningful CDAD in the [001] substrate mirror plane, but in the absence of a comparative dataset from the second enantiomer this effect is less convincing. In the case of the complex alaninate phase, reliable molecule-induced CDAD was seen in the N 1s data for both enantiomers, as shown in figure 7; in this case a photon energy of 450 eV was used to produce a similar photoelectron kinetic energy to that of the C 1s data shown in figures 3–6. Here too, the largest CDAD effects occur out of the substrate mirror planes and have the same sign for both enantiomers, but in the mirror planes there are significant residual CDAD signals having the required opposite signs. Figure 7 also shows CDAD data for O 1s photoemission from the (3 × 2) phase at a photon energy of 570 eV (and hence a similar photoelectron kinetic energy) for which a complete and reliable data set is available; in this case any residual CDAD in the substrate mirror planes is

very marginal in its significance. Of course, there are two inequivalently located O atoms in the adsorbed alaninate (figure 1), but in the absence of any clear chemical shift in the associated O 1s emission, the data represent an incoherent sum of emission from the two sites; this may well contribute to the lack of significant detectable molecule-induced CDAD in this experiment.

4. Discussion

The goal of this investigation was to try to establish whether CDAD in photoemission from the core levels of atoms in adsorbed chiral molecular species, when measured in an appropriate geometry, may provide a generally viable spectral fingerprint of the molecular chirality. Our results show that there is indeed a measurable effect, and define some of the ways in which this may be optimized. Our experiments focused on the (3×2) surface phase of adsorbed alaninate for which we believe we have a reasonable understanding of the structure. However, we actually find somewhat stronger CDAD derived from the molecular chirality from the complex phase for which the detailed structure is much less well understood. In some ways, one might therefore argue that the choice of the (3×2) alaninate phase on Cu(1 1 0) is a poor choice to evaluate this effect. Perhaps the structure of this system is too close to having local mirror symmetry (see figure 1) to illustrate the effect well. On the other hand, the ultimate objective of this experiment is to try to evaluate the CDAD effect, measured in a substrate mirror plane, as a general and simple spectral fingerprint of adsorbate molecular chirality. Clearly, if any chiral molecular adsorbate gives very weak CDAD, this generality of application is undermined. The fact that the molecule-induced CDAD is sometimes very weak, and that the CDAD resulting from instrumental misalignments of only a few degrees in azimuth is comparably strong, does suggest that, at the very least, CDAD cannot be a simple spectral fingerprint. Clearly, for an unknown system, one must either be very sure that the experimental geometry is such as to ensure that only chiral molecule effects are seen, or perform some kind of angular scans around the special experimental geometries of interest in order to distinguish the two effects. Any need to perform such angular scans increases the complexity of the experiment, which then ceases to provide a simple spectral fingerprint.

Of course, this problem might be overcome if there was some generally applicable set of conditions which ensure a relatively large molecular CDAD effect. Is there one specific atomic site within the molecule which is more favourable, or can one define the optimum polar-emission angle or photoelectron kinetic energy within the substrate mirror plane? On the basis of our limited data for the two structural phases of alanine on Cu(1 1 0) no such simple rules emerge. One parameter which might be important and which is not explored in the experimental results shown here is the photoelectron energy. Insofar as the CDAD effect is closely related to photoelectron diffraction, one may expect that low kinetic energies would be favoured; at high energies electron scattering cross-sections are small other than in forward scattering (near 0° scattering angle). In backscattering photoelectron diffraction (dominated by substrate atom backscattering) the effects are typically largest around 50–200 eV. Measurements at lower energies are generally not used so much because (as in quantitative LEED structure determinations) the multiple scattering calculations are generally thought to become less reliable at very low energies. On the other hand, for low atomic number elements such as C, N and O, the back-scattering cross-sections fall off quite strongly even at the upper end of this energy range, so even lower photoelectron energies may be favoured. The experimental results shown here involve photoelectron energies

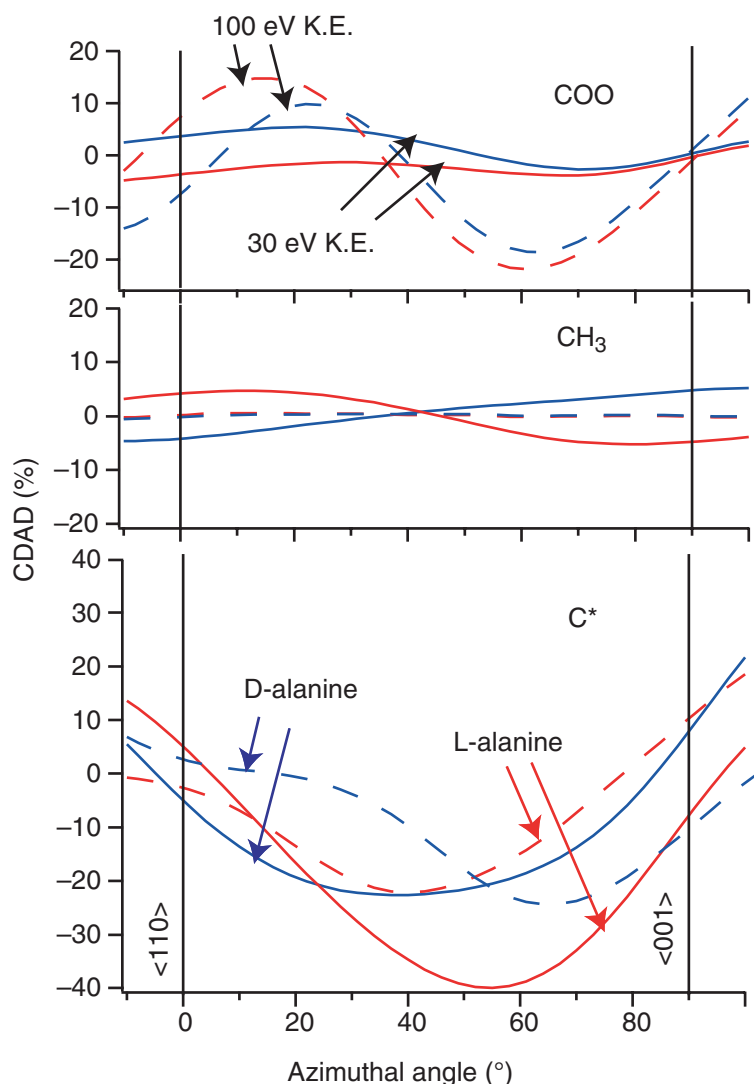


Figure 8. Theoretical predictions of the azimuthal angle dependence of C 1s CDAD from the (3×2) phase of alanine on Cu(1 1 0) at 30° polar emission angle at 30 eV photoelectron kinetic energy (cf figure 4) and at a higher kinetic energy of 100 eV.

of only around 20–30 eV; a small number of experimental measurements were made at higher photoelectron energies, and failed to show reliable molecule-induced CDAD, but it is difficult to know if this is a general result. In this respect, theoretical simulations may prove useful (being untroubled by the many experimental problems which limit reliability) and figure 8 compares the calculated CDAD as shown in figure 3 (with a nominal 30 eV kinetic energy) with calculations for the same structure and experimental geometry but at the higher photoelectron energy of 100 eV. There is no obvious simple trend. For the methyl C the CDAD almost vanishes at the higher energy both in and out of the substrate mirror planes. For the other two C emitters, the size of the CDAD is similar in the mirror planes for the two energies, although the relative size of the CDAD effect out of the mirror planes switches between the two emitter sites. One might infer that the very weak CDAD from the methyl C is consistent with the fact that this C atom

is furthest from the surface. Any CDAD for this emitter thus relies on the weak backscattering of the nearest-neighbour carbon (C*) atom, while the other emitters will have the possibility of contributions from forward scattering or substrate atom backscattering. This would imply that, while CDAD may be observed at higher (tens of eV) energies, the lowest energies give the best chance of observing the effect. In this regard it is notable that in all gas-phase measurements of CDAD from a chiral molecule reported to date, the effect was only seen at very low photoelectron energies (5–10 eV) [10], [15]–[17].

In view of this rather cautious conclusion regarding the utility of CDAD to characterize the presence of a single enantiomer of a chiral species on the surface one may consider alternative approaches. Perhaps the simplest situation is when the adsorbed chiral molecules form a single domain of a long-range-ordered phase which is itself chiral (i.e. with no occupation of the mirror-image domain). In this case, a simple LEED pattern reveals the reduced symmetry and provides a very simple means of identifying the presence of a single enantiomer (at least in the ordered part of the surface). Indeed, the $\begin{pmatrix} 2 & -2 \\ 5 & 3 \end{pmatrix}$ and $\begin{pmatrix} 5 & -3 \\ 2 & 2 \end{pmatrix}$ phases of the two enantiomers of alanine on Cu(1 1 0) have precisely this property [8]. Clearly, however, this is not a generally applicable method for identifying the presence of chiral species on a surface. In contrast to LEED, which identifies the long-range order, local structural techniques offer a means of identifying the reduced symmetry of individual adsorbed molecules; in particular, photoelectron diffraction provides real-space directional information which can provide this information. Indeed, in its high energy forward scattering form—so-called x-ray photoelectron diffraction (XPD)—this method has been shown to be a viable means of determining the orientation and aspects of the internal conformation of adsorbed chiral molecules even when there is no long-range ordering [44, 45]. While these studies were conducted on known adsorbates which greatly simplified the interpretation of the data, the reduced symmetry characteristic of a single adsorbed enantiomer is visible in the raw data, so one could imagine that this method would also provide a general means of identifying such adsorbates. On the other hand, collecting the wide range of emission angles which characterize such XPD experiments is extremely time-consuming and certainly not a simple spectral fingerprint.

Of course, traditional circular dichroism experiments measure the absorption of circularly polarized radiation, and even for sub-monolayer coverages of adsorbed molecules, absorption measurements in the x-ray range are perfectly possible by monitoring a signal related to the core-hole decay. This is the basis of near-edge x-ray absorption fine structure (NEXAFS) studies, which provide a spectral fingerprint of molecular adsorbates. In fact the possibility of using CD in NEXAFS for adsorbed chiral species (notably of small amino acids) has been explored theoretically [46]. These calculations indicate, however, that the effect is very small ($\ll 1\%$) and so is unlikely to provide a viable approach. In the experimental work reported here, we did conduct limited tests of CD in NEXAFS for adsorbed alanine but failed to detect any significant effect, although our investigation could not exclude the very weak effects predicted in these theoretical calculations.

In the discussion so far, we have focused on CDAD as a means of identifying chiral adsorbate species on a surface. In discussing the symmetry implications of adsorbing such a molecule on the surface, however, we have pointed out that formally the presence of such a species renders the whole surface chiral, as even the substrate atoms close to the adsorbate have local surroundings for which there is no mirror equivalent. In this context, one should note that even in the absence of an adsorbed chiral species a surface may itself be chiral if it is mis-cut relative to a

low-index plane in an azimuthal orientation away from any of the mirror symmetry planes of the underlying bulk crystal. Indeed, there is significant interest in such stepped and kinked surfaces as a potential means of creating enantioselective heterogeneous catalysts. There is even evidence that a chiral molecule adsorbed on a surface may, in some circumstances, cause a local faceting of the underlying surface to such a low-symmetry chiral structure [47]. What are the implications of such a surface for CDAD? In the case of the chiral surface structure in the absence of a chiral adsorbate, it is clear that the situation is similar to that of a chiral adsorbate on a non-chiral surface. The outermost atomic layer steps and kinks play a similar role to the adsorbed molecule in the CDAD, so they will lead to a residual CDAD signal in a mirror plane of the underlying substrate. Indeed, this effect seems to have been seen in a valence photoemission CDAD study of a Pt(6 4 3) surface [48]; the authors note that in azimuthal scans of the CDAD the dichroism almost vanishes in the $\langle 1\ 1\ 2 \rangle$ mirror symmetry planes of the substrate. This wording could equally well describe many of our experimental and theoretical results for alanine adsorbed on Cu(1 1 0). One important implication of this conclusion, however, is that if one adsorbs chiral molecules onto a chiral surface one will observe residual CDAD in the mirror plane of the substrate, but this will also be the case if one adsorbs a non-chiral molecule onto such a chiral surface. In this way, the use of a chiral surface (of potential interest in studying enantioselective chemistry on the surface) may make it more difficult for CDAD to provide a reliable guide as to whether a single enantiomer of a product is really present on the surface. The use of core-level photoemission CDAD clearly does provide a more local probe of the molecule which reduces this problem, but scattering contributions from substrate atoms at the stepped and kinked surface may still induce CDAD into the adsorbate photoemission.

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