

Atom-Specific Identification of Adsorbed Chiral Molecules by Photoemission

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The study of chiral adsorbed molecules is important for an analysis of enantioselectivity in heterogeneous catalysis. Here we show that such molecules can be identified through circular dichroism in core-level photoemission arising from the chiral carbon atoms in stereoisomers of 2,3-butanediol molecules adsorbed on Si(100), using circularly polarized x rays. The asymmetry in the carbon 1s intensity excited by right and left circularly polarized light is readily observed, and changes sign with the helicity of the radiation or handedness of the enantiomers; it is absent in the achiral form of the molecule. This observation demonstrates the possibility of determining molecular chirality in the adsorbed phase.

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Ever since Pasteur discovered the handedness in the optical activity of sodium ammonium tartrate [1], chirality has been recognized as a most important aspect of molecular structure. Its implications in biochemistry are far reaching since most biomaterials exhibit predominance for a single enantiomer. Hence the importance of the synthesis and separation of pure enantiomers has been well recognized [2]. Heterogeneous catalytic processes for enantioselective synthesis have important advantages over conventional homogeneous ones [3]. The occurrence of chiral preference may be an important step in the heterogeneous catalytic conversion of prochiral reagents into one of possible optical isomers. Such enantioselectivity is usually induced by adsorbing chiral molecules onto catalytically active surfaces [4]. This is why a characterization of chiral centers in adsorbed molecules is desirable. Certain spatial arrangements of chiral molecules on surfaces have been studied in scanning tunneling microscopy, and a preferred chemical interaction between pairs of stereoisomers was found [5]. A large asymmetry in the scattering of polarized slow electrons by films of chiral organic molecules was observed, and attributed to quantum interference on the scale of supramolecular lengths [6], and an intriguing connection between magnetism and the chiral nature of molecules in self-assembled monolayers was found [7]. However, the direct detection of chiral centers by means of electron spectroscopy, widely used for surface studies, has so far proven elusive. Yet this is a desirable goal since it would provide an atom-specific means of detecting the presence of chiral centers in adsorbed molecules, either in an adsorbate that is chiral already, or in which such a feature is produced by adsorption-induced deformation. Theoretical treatments have predicted that spatially oriented chiral molecules, such as may be present in adsorbed layers, should show circular dichroism (CD), i.e., a dependence of intensity on helicity of the light, in the angular distribution of photoelectrons [8]. Even in randomly oriented chiral molecules in the gas phase, such an effect was

predicted and recently experimentally verified both in core-level and valence-level photoemission [9]. The complication for detecting circular dichroism in adsorbed species lies in the fact that a "handed experimental geometry" may also induce a dichroic signal which is entirely unrelated to the chirality of the adsorbate. Here we show, by a suitable choice of geometry, and through a comparison of different (chiral and achiral) stereoisomers of 2,3-butanediol adsorbed on Si(100), circular dichroism in core-level photoemission due to a chiral center.

The CD measurement has been performed using right and left circularly polarized (RCP and LCP) light at the UE56/2-PGM1 beam line at BESSY II [10]. Photoelectron signals ejected from C 1s core levels were recorded using an angle-resolved electron analyzer (OMICRON AR65); some data were recorded with an angular dispersive analyzer (PHOIBOS 100, SPECS GmbH). The Si(100) surface was cleaned by flashing a few times to 1400 K after several hours of outgassing at 800 K. The 2,3-butanediol was adsorbed on the Si(100) surface to a saturated amount at room temperature and its coverage is estimated to be about 0.25 monolayer [11]. Data were mainly recorded from a Si(100) surface deliberately miscut by 4° in order to provide only one orientation of the surface dimers; however, data from surfaces where both orientations were present gave identical results. Data were recorded under a few different azimuthal directions of the emitted photoelectrons.

It is advantageous to use 2,3-butanediol for such a study, since this molecule has both chiral and achiral carbon atoms, as evident from Fig. 1(a) which shows two enantiomers [(*S,S*) and (*R,R*) forms]; moreover, an achiral (*R,S*) stereoisomer exists. A suitable substrate for the adsorption of molecules is Si(100) which offers the well-known dimer reaction site, and the adsorption of simple alcohols on this surface has been investigated before [12]. Upon adsorption at room temperature, the O-H bonds are spontaneously broken, and the molecule is supposed to

take a bridging position on the Si(100) surface as shown in Fig. 1(b) [11]. Since 2,3-butanediol has two identical (COH-CH₃) units, the molecule is expected to form a six-membered ring with C₂ rotational symmetry on the Si(100) (2 × 1) surface via bonding to a Si dimer. This interaction is analogous to the (4 + 2) cycloaddition or Diels-Alder reactions [13]. Thus, a stable configuration is provided to observe circular dichroism in a two-dimensional system, without a change in the configuration around the chiral centers.

The two types of carbon atoms in 2,3-butanediol, i.e., the chiral one bonded to the oxygen atom, and the achiral one in the CH₃ group, are easily distinguished since they exhibit a difference in C 1s binding energies of 1.3 eV, due to their different chemical environment. This provides the opportunity to measure an atom-specific CD effect. A schematic sketch of the experimental geometry is shown in Fig. 2(a), where \mathbf{n} is the surface normal, \mathbf{q} the direction of light incidence, and \mathbf{k} the direction of electron emission. The data for the C 1s core level from (*R,R*) 2,3-butanediol under RCP (blue) and LCP (red) light are shown in the topmost spectra of Fig. 2(b). These spectra were recorded in normal emission at a photon energy of $h\nu = 330$ eV with an incident angle of 54° from the surface normal. A sizeable dichroic effect occurs in the peak arising from the carbon atom in the chiral center. As seen from the middle

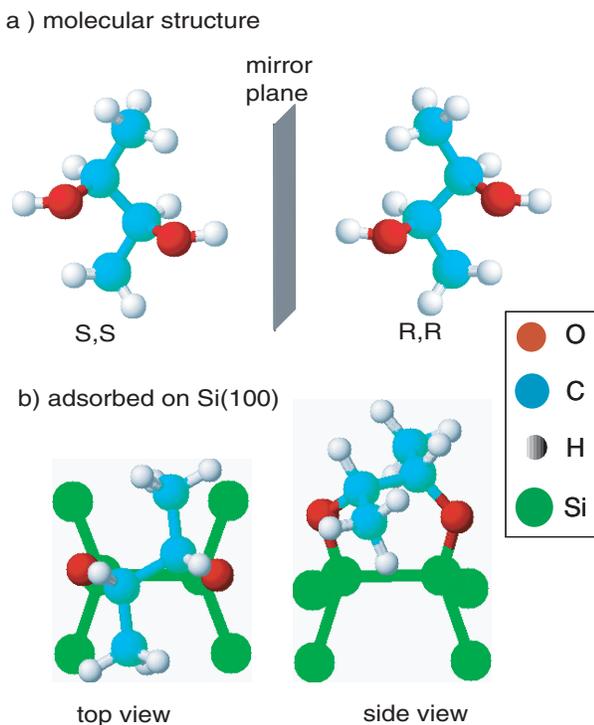


FIG. 1 (color online). Structural models before and after the adsorption. (a) Molecular models of enantiomers of the *S,S* (left) and *R,R* (right) forms of 2,3-butanediol. (b) Adsorption geometry for (*S,S*) 2,3-butanediol on a Si(100) surface as inferred from core- and valence-level photoemission (Ref. [10])

spectra, an asymmetry of equal magnitude but opposite sign occurs when the (*S,S*) enantiomer, the mirror image of the (*R,R*) form, is investigated. Finally, no asymmetry occurs when the achiral (*R,S*) isomer is adsorbed on the surface as shown in the bottom spectra of Fig. 2(b). The reversal of asymmetry in going from the *R,R* to the *S,S* enantiomer is seen in the difference spectra shown in Fig. 2(c). These observations are a clear proof that this dichroic signal is caused by the chiral nature of the environment of the respective carbon atom as discussed in more detail below [14].

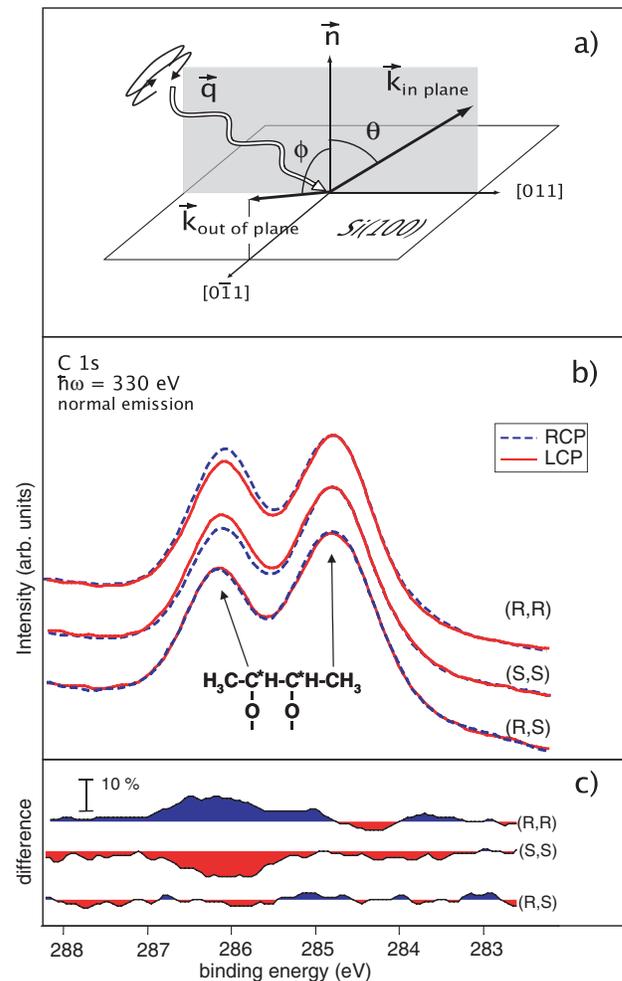


FIG. 2 (color online). (a) Schematic view of the experimental geometry; \mathbf{n} is the surface normal, \mathbf{q} the direction of light incidence, and \mathbf{k} the direction of electron emission. (b) Photoelectron spectra of the carbon 1s core levels for the adsorbed stereoisomers of 2,3-butanediol excited by right (dashed line, blue online) and left circularly polarized (solid line, red online) light. Dichroism is observed on the higher-binding energy component attributed to emission from the carbon atoms in the chiral center from the (*R,R*) and (*S,S*) forms. The dichroic effect changes sign either with photon polarization or molecular handedness. No dichroism is observed in the achiral (*R,S*) form. (c) Difference signal for the three stereoisomers.

What is the nature of the electronic transition giving rise to the observed asymmetry in the present photoemission intensity? The C 1s core level is unlikely to “feel” the chiral nature of its molecular environment. The asymmetry then arises from final state elastic electron scattering effects, which may reveal themselves in photoelectron diffraction experiments [15]. In an equivalent formulation, they are related to a transition of the photoexcited electron from the core level into an unoccupied or continuum state which belongs to one of the irreducible representations of the molecule’s (or the adsorption complex’s) point group. The influence of the latter determines the sign and magnitude of the circular dichroism [16]. Considering the matrix element governing the photoemission intensity, the strongest transitions will occur into those unoccupied levels that are localized near the core-ionized carbon atom, i.e., those that exhibit chirality as a result of the electronic charge distribution around them. Depending on the nature of the final state, a dichroic signal may thus also occur in core-level photoemission from atoms which do not form part of the chiral center. A similar interpretation has been applied to the gas phase photoemission results [9]. The effect is proportional to the interference of pairs of dipole matrix elements which differ by the signs of all projections of orbital momenta. For nonchiral molecules having a plane of symmetry, these differences are equal to zero. In fact, no dichroism is found in the achiral stereoisomer (bottom spectra of Fig. 2) where the asymmetry in emission from the *R* and *S* environments of the carbon atoms in the molecule cancels.

In an analysis of CD in core-level photoemission, one has to take into account an effect arising from the experimental geometry, however. It is well known that strong circular dichroism can be observed even in adsorbed achiral molecules, e.g., linear ones, such as CO/Pd(111) [17]. The reason for this is the presence of a handedness in the combined system of incoming photons, emitted photoelectrons and the orientation of the molecule. Thus even if the molecule has no “natural” chirality, it is possible to induce dichroism through the handedness of the experimental geometry. This CD in angular distribution (“geometry-induced” CD) has been extensively studied by Schönhense and co-workers [14,17]. It is very important to distinguish, for a possible use of core-level photoemission to detect chiral centers, between the CD effect arising from the chiral center in the molecule, or from the experimental geometry. That the asymmetries in Fig. 2 indeed arise from the chiral centers in the molecule can be demonstrated by the following argument. First, geometry-induced CD in an emission direction \mathbf{k} in the plane defined by the incident light vector \mathbf{q} and the surface normal \mathbf{n} will vanish [Fig. 3(a)], since no handedness is present in this experimental (“coplanar”) geometry [14]. This is the reason for the choice of our measurement geometry, the highest molecular rotation axis being collinear to the surface

normal. Second, since in an optical dipole transition, parity-violating processes are negligible, the result of an experiment such as that shown in Fig. 2 must be invariant upon application of a parity operation which changes both the photon helicity and the handedness of the molecule. This is clearly borne out by the results in Fig. 2, showing that it is indeed the chiral nature of the molecule that gives rise to the observed dichroism.

A further argument to exclude the influence of experimental handedness comes from the intensity asymmetry observed under different photoelectron emission directions at a fixed photon-incidence angle. The geometry was again chosen such that the axes for \mathbf{q} , \mathbf{n} , and \mathbf{k} are coplanar [“in-plane geometry,” Fig. 2(a)]. It is straightforward to extract the change in relative intensity of the two C 1s lines upon changing the polarization of the light. The magnitude of circular dichroism is determined by evaluating the asymmetry $\mathbf{A} = (I^{RCP} - I^{LCP}) / (I^{RCP} + I^{LCP})$ where I is the intensity of the core level for a circular polarization of synchrotron light. We find that the asymmetry value is reversed with polar angles (Θ) in going from the (*R*, *R*) to the (*S*, *S*) enantiomer [Fig. 3(a)]. Calculations predict that the dichroism caused by the handed geometry may occur in an oriented nonlinear molecule even in the coplanar experimental geometry [16]; hence, we might observe such effect in this polar angular distribution. However, the asymmetry reversal for two different enantiomers reveals the chirality in the molecular environment as the source of CD. The emission angle clearly influences the magnitude of the asymmetry. It is reassuring that the CD effect of two enantiomers is almost equal but opposite. In a direction (Φ) perpendicular to the plane of incidence, the actual signal may be influenced by the geometry-induced CD effect since the geometry is not coplanar. Our data for the out-of-plane measurements [Fig. 3(b)] show that the dichroism for both enantiomers here has the same sign away from the

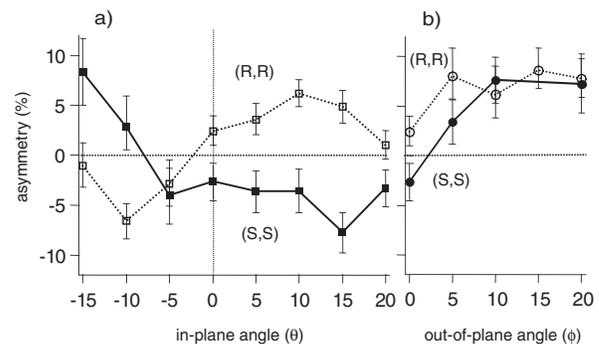


FIG. 3. (a) CD effect in the C 1s level of the enantiomers of 2,3-butanediol measured for emission angles (θ) in-plane, i.e., within the plane of incidence and (b) out of plane, i.e., in the plane perpendicular to the plane of incidence (ϕ). Note the large asymmetry and its reversal upon switching the molecular handedness in (a). Error bars mean statistical deviation in the fitting of each peak area.

surface normal, which may be taken as an indication that the handedness of the experimental geometry dominates the dichroism signal under these experimental conditions.

In a recent study of the adsorption of *D* and *L* alanine, the simplest chiral amino acid, on Cu(110), Polcik *et al.* have measured circular dichroism and compared their data with multiple scattering photoelectron diffraction calculations [15]. They investigated the dichroism induced by changing the substrate crystal azimuth in off-normal emission, and observed a rather large (up to 30%) geometry-induced CD effect away from substrate mirror planes, for emission from a carbon atom in the chiral center, and a dichroism comparable in magnitude to our observation (on the order of 4%) in the mirror planes, in agreement with multiple scattering photoelectron diffraction calculations. These data suggest that dichroism induced by the chiral nature of the environment of the carbon atom may be weak compared to that induced by the experimental geometry, and may thus limit the utility of the method as a spectroscopic probe of chirality. Data such as in Fig. 2 recorded in normal emission geometry preclude complications arising from the breaking of symmetry by the substrate and rule out a disturbing influence of the handedness of the experimental geometry. The detection of the chiral character of an adsorbed species through dichroism in core-level photoemission will then depend on the strength of the respective transition matrix element, about which little is known at present. Indeed, more theoretical work to provide a comprehensive picture of the physical processes involved, and treatments of electron scattering from chiral molecules in general [6,7], are highly desirable.

In summary, we observe a clear circular dichroism in core-level photoelectrons from the two enantiomers of 2,3-butanediol adsorbed on Si(100). We are able to distinguish this effect from a dichroism induced by the handedness of geometric arrangement of the incident electromagnetic radiation and the outgoing photoelectron path, since the asymmetry changes sign with enantiomer and photon polarization. In view of the increasing importance of an analysis of biologically active surface species, our observation may provide a path to analyzing chiral centers in complex adsorbed molecules using photoemission spectroscopy.

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