

Circular dichroism in core level photoemission from an adsorbed chiral molecule

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There has been growing interest in the last few years in the properties of chiral molecules adsorbed on surfaces, motivated in part by the potential practical importance of producing molecular products of a single 'handedness' (enantioselective) by heterogeneous catalysis. In such studies a simple spectroscopic measurement, which could establish whether or not the surface species (which may be reaction intermediates of unknown identity) are predominantly of a single chirality, would be of great value. Conventional optical absorption measurements on sub-monolayer coverages of adsorbed molecules which exploit the circular dichroism (a difference in absorption for left- and right-circularly polarised radiation) in this spectral range are unlikely to be fruitful. However, spatially oriented chiral molecules, such as those adsorbed on a surface, should show circular dichroism in the angular distribution (CDAD) of photoelectrons emitted from these species [1, 2]. Indeed, such an effect has recently been observed [3] even for randomly oriented chiral molecules in the gas phase. CDAD from adsorbate core levels also has the potential advantage of being specific to the surface chemical species on the surface, even if its identity is unknown, through photoelectron binding energy core level shifts.

To explore this idea we have investigated experimentally a model system supported by theoretical multiple scattering calculations. The system investigated is alanine, the simplest chiral amino acid, adsorbed on Cu(110); we have also investigated the local adsorption geometry of this species and the simpler species, glycine, by photoelectron diffraction [4, 5]. An important aspect of CDAD, however, is that even non-chiral surfaces give rise to a significant signal if the geometry of the experiment is chiral [6]. If the plane defined by the incident (circularly polarised) light and the photoelectron collection direction does not correspond to a mirror symmetry plane of the sample, the experiments conducted with opposite circular polarisations will not be equivalent and so a circular dichroism signal will be observed. This CDAD effect (of magnitude up to 50% or more) from core levels of atoms in non-chiral surfaces is well-established from substrate atoms (e.g. Si(100) [7, 8] and W(110) [9]), from adsorbed atoms (e.g. Rb and K [10]) and from adsorbed linear molecules (notably CO [11, 12, 13] and NO [14]). A key question which we aim to answer, therefore, is this: can a CDAD effect due to adsorbate chirality clearly be distinguished from that due to these other effects?

Our results show that these two sources of CDAD *can* be separated, and indeed that adsorption onto the surface creates a system in which *all* the C atoms of the alanine reflect the chirality of the adsorbate on the surface (not just the C* 'chiral centre' of the gas-phase NH₂CH₃C*HCOOH molecule). However, the results (supported by

theoretical calculations) also show that the CDAD associated with chiral experimental geometries is generally much larger than that due to the adsorbed molecule, so great care is needed to ensure the result is meaningful. As such, it seems doubtful that such measurements can provide the routine spectral fingerprint which could prove so useful. A brief review of alternative possibilities appears to offer no more promising route to this goal.

References

- 1 B. Ritchie, Phys. Rev. A 12, 567 (1975); 13, 1411 (1976)
- 2 N.A Cherepkov, Chem. Phys. Lett. 87, 344 (1982)
- 3 U. Hergenbahn *et al.*, J. Chem. Phys. submitted for publication
- 4 N.A. Booth, D.P. Woodruff, O. Schaff, T. Gießel, R. Lindsay, P. Baumgärtel, A.M. Bradshaw, Surf. Sci 397 (1998) 258
- 5 J.-H. Kang, R. L. Toomes, M. Polcik, M. Kittel, J.-T Hoefft, V. Efstathiou, D. P. Woodruff and A. M. Bradshaw, J.Chem.Phys. 118 (2003) 6059
- 6 G. Schönhense, Physica Scripta T31, 255 (1990)
- 7 H. Diamon *et al.*, Jpn. J. Appl. Phys. 32, L1480 (1993)
- 8 A.P. Kaduwela *et al.*, Phys. Rev. B 52, 14927 (1995)
- 9 R.X. Ynzunza *et al.*, J. Electr. Spect. Rel. Phenom. 106, 7 (2000)
- 10 A. Oelsner *et al.*, Surf. Sci. 331-333, 349 (1995)
- 11 J. Bansmann *et al.*, Phys. Rev. B 46, 13496 (1992)
- 12 J. Bansmann *et al.*, Z. Phys. D 33, 257 (1995)
- 13 C. Westphal *et al.*, Phys. Rev. B 50, 6203 (1994)
- 14 G.H. Fecher *et al.*, J. Elect. Spect. Rel. Phenom. 76, 97 (1995)