COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Chiral discrimination within disordered adlayers on metal surfaces

Andrew Mulligan,[a] Ian Lane,[b] Gilles B. D. Rousseau,[a] Lutz Hecht,[a] Shona M. Johnston,[a] David Lennon[a] and Malcolm Kadodwala*[a]

[a] *Department of Chemistry Joseph Black Building, University of Glasgow, Glasgow, UK G12 8QQ. E-mail: malcolmk@chem.gla.ac.uk*

[b] *Department of Chemistry David Keir Building, Queen's University of Belfast, Belfast, UK BT9 5AG. E-mail: i.lane@qub.ac.uk*

Received (in Cambridge, UK) 1st July 2004, Accepted 5th August 2004
First published as an Advance Article on the web 13th September 2004

Using a novel non-linear optical technique enantiomeric excess within a translationally disordered overlayer on a metal surface has been monitored for the first time.

Understanding the behaviour of chiral adsorbates on metal surfaces is crucial for the development of promising technologies such as enantioselective metal-based heterogeneous catalysis and chiral recognition.[1] Recently UHV surface science studies have been performed on model systems.[2] The range of problems that can be addressed by these studies is limited by the need to use high-resolution scanning tunnelling microscopy (STM) images to achieve chiral discrimination within adsorbed layers. Chiral discrimination is achieved by inferring absolute configuration from high-resolution STM images: this can be done at low coverage where a discrete small single (immobile) molecule can be imaged,[3] or at higher coverage in systems where ordered homochiral domains are observed.[4,5] Unfortunately, high-resolution STM images cannot always be obtained for translationally disordered and complex overlayers, which are particularly relevant for catalytic systems since adsorbed chiral modifiers such as cinchona alkaloids, are not believed to form ordered arrays on metal surfaces.[6] An optical probe for surface chirality would therefore ideally complement existing scanning probe microscopy techniques. Conventional spectroscopic chiral probes used in the bulk phase are generally based on monitoring very small asymmetries: typically $<0.1\%$ in circular dichroism (CD) absorption measurements (*e.g.* UV-CD and VCD). These techniques are not well suited to surfaces because the small quantity of adsorbed species and low asymmetries mean that the magnitude of the absolute difference in signal is often below the detection limit. Second order non-linear optical processes are ideally suited to probe surfaces, as they are forbidden within the dipole approximation in media with inversion symmetry. Consequently, the SH generation process exhibits an intrinsic sensitivity to symmetry breaking interfaces. The intensity of the SH signal is proportional to the second order susceptibility tensor $\chi^{(2)}$ of the interface.In the extension of SH to enantiomer sensitive (ES)-SH proposed here, asymmetries of tens of percent can be observed for different enantiomers. The ES-SH technique is highly flexible and has been applied to liquid–insulator and liquid–liquid interfaces.[7] However, it has never been applied to study chiral adsorbates on metal surfaces.

We demonstrate here that, using ES-SH measurements, enantiomer discrimination can be achieved for disordered and complex overlayers. This novel application of surface second harmonic generation provides a quantitative, non-invasive and generic probe of chiral adsorbate-metal systems.

Experiments were performed in a UHV system in which the surfaces of Cu(111) were cleaned and characterised. Cleaning was achieved by repeated cycles of Ar^+ sputtering and annealing. Monitoring of crystal quality and characterisation of overlayers was achieved using a combination of low energy electron diffraction (LEED) and x-ray photoelectron spectroscopy (XPS). ES-SH measurements were performed using 8–12 ns pulses of fundamental Nd:YAG laser (Spectra Physics Quanta Ray) 1064 nm radiation at a repetition rate of 10 Hz and $\sim$3.6 mJ pulse^{-1}. The beam was defocused (10 mm diameter) and was incident on the crystal at 60° with respect to the surface normal, the incident polarisation was varied using a $\lambda/2$ plate. The SH signal was monitored at 60° with respect to the surface normal: it first passed through a polariser before being focused into a spectrograph and then detected on an intensified CCD camera.

The model systems we have used in this study are disordered monolayers of (*R*)-, (*S*)- and racemic 2-butanol on Cu(111). Linearly polarised fundamental radiation (1064 nm) is incident on the surface, and changes to the intensity of the out-going SH light (532 nm) induced by the chiral adsorbate layer are monitored. Our measurements are related to those performed to monitor polarisation rotation in SH from chiral overlayers.[8] Large differences in the rotation of the SH polarisation between pairs of enantiomers can be observed using these methods. Applying such SH techniques is not as straightforward for a metal surface as for liquid and insulator interfaces. In contrast to insulator interfaces, the SH signal from an adsorbate-metal interface has two contributions: a major one from the metal–adsorbate interface (SH_{metal}) and a minor one from the adsorbate–vacuum surface (SH_{ads}). The two contributions can have both different magnitudes and phases. The SH_{metal} component reflects the electronic structure of the metal, and changes in it upon adsorption reflect adsorbate-induced changes in the electronic structure of the metal. The relative sizes of SH_{metal} and SH_{ads} depend strongly on both the polarisation of the incident fundamental light and the polarisation at which the overall SH signal is detected, but for almost all possible combinations of incident light and detection polarisations, $SH_{metal} \gg SH_{ads}$.[9,10] Under these conditions a chiral dependence of the SH signal would only be observed if the electronic structure of the metal surface had been imbued with chiral character by the adsorbate. However, with s-polarised fundamental radiation (perpendicular to the plane of incidence, hence parallel to the surface) and detecting at, or close to, s-polarisation, the SH_{metal} is reduced to such an extent that it is of a similar magnitude to SH_{ads}.[10] Since the layers are disordered, and enantiomers will have identical adsorption geometries on an achiral substrate, differences observed in the overall SH intensity must reflect an enantiomer dependence in the SH_{ads} contribution.

Preliminary temperature programmed desorption (TPD) and UV photoelectron spectroscopy (UPS) experiments demonstrated that 2-butanol interacts weakly with Cu(111). UPS data showed that upon adsorption the electronic structure of the molecule was not significant perturbed from the gas phase, and that it did not dissociate. TPD data confirmed the weakness of the interaction, with the monolayer desorbing intact without dissociation at 211 K. We believe that 2-butanol interacts with the Cu(111) surface via the oxygen atom, and the C–O bond is close to perpendicular to the surface, this assertion is based on previous studies of 2-butanol and other alcohols.[11] Monolayers of (*R*)-, (*S*)- and racemic 2-butanol were prepared by annealing condensed layers, deposited at 110 K, to a temperature of 168 K which was sufficient to desorb only the multilayers. XPS was used to confirm that (*R*)-, (*S*)- and racemic 2-butanol overlayers all had identical coverages. Although the adsorbed molecules have a well-defined adsorption geometry,

DOI: 10.1039/b409886b

the lack of any ordered LEED patterns indicated that the three overlayers display no long-range 2-D ordering.

In this experiment we have monitored the SH intensity at two outgoing polarisations, +35° (I_{35}) and −55° (I_{-55}) with respect to the s-polarisation plane. Based on crystal symmetry arguments, signals at +35° should have lower contributions from the metal surface $\chi^{(2)}$, and hence a smaller SH_{metal}, than those collected at −55°.[10] This prediction is verified by the clean surface measurements shown in Fig. 1, the SH signal at +35° is significantly smaller than that at −55° with a I_{+35}/I_{-55} ratio of 0.088 ± 0.002. This ratio, and similar ones for 2-butanol monolayers, are averages of values obtained from five freshly prepared surfaces, the quoted errors are corresponding to one standard deviation in ratios.

For monolayers of racemic, (*R*)- and (*S*)-2-butanol there is no measurable change in the SH signal at −55° compared to the clean surface. Two conclusions can be drawn from this observation: firstly any contribution to the overall SH signal due to the adsorbate layer is too small to be discriminated from the large background of the metal signal and secondly the $\chi^{(2)}$ of the metal surface remains unaffected by the chiral adsorbate. This indicates that the surface electronic structure is not strongly perturbed by adsorption (in agreement with the low desorption temperature) and that the electronic structure of the metal has not been imbued with chirality by the adsorbate. This last conclusion is supported by measurements with in-going p-polarised (parallel to the plane of incidence) radiation. In those measurements the overall SH signals which are completely dominated by SH_{metal} contributions[10] display no enantiomer dependence. In contrast to the −55° signals however, those collected at +35° show a significant increase in SH intensity measured from adsorbate covered surfaces when compared to the clean surface (data not shown). The contribution made by the adsorbate layer to the overall SH signal is measurable at +35° because it is much less obscured by the underlying metal background signal. We can therefore use the "metal" signal at −55° to normalize the 35° " adsorbate" signal which was collected immediately afterwards, consequently changes in I_{+35}/I_{-55} ratios between overlayers reflect enantiomer dependent changes in the SH_{ads} contribution to the overall SH signal.

The adsorbate contribution to the overall SH signal at +35° is different for all three surfaces, as seen in Fig. 1, with I_{+35}/I_{-55} ratios of 0.108 ± 0.002, 0.100 ± 0.002 and 0.118 ± 0.002 for racemic, (*R*)- and (*S*)-monolayers respectively. The observation of different ratios for the three layers, and the fact that the average of the ratios for the (*R*)- and (*S*)-monolayers, 0.109, is identical within experimental error to the racemic value (0.108 ± 0.002), are entirely consistent with an enantiomer specific measurement.

The observed difference in the SH_{ads} component for the (*R*)- and (*S*)-enantiomers should arise from the rotation in the polarisation of the SH_{ads} component. Pairs of enantiomers rotate the polarisation of SH_{ads} in opposing senses, with the racemic mixture inducing no rotation. Such rotations in the SH_{ads} signal would result in one enantiomer having a larger SH_{ads} contribution as observed.

The results of the current study clearly demonstrate that by using experimental conditions which minimise the SH_{metal} contribution to the overall SH signal, a change in the SH intensity can be detected that enables enantiomeric excess within an overlayer to be observed. Based on the precision of our measurements we estimate that enantiomeric excesses of >22% could be detected in the current 2-butanol/Cu(111) system. Since we have not currently optimised the measurement, specifically determining the most favourable pair of out-going polarisations at which measurements could be made, it is likely that enantiomeric excesses <22% could potentially be measured. This application of the ES-SH technique is therefore a significant improvement on current probes of enantiomers on metal surfaces. Like conventional SH measurements, ES-SH should be applicable to both non-UHV environments (*e.g.* liquid–metal interfaces) and to non-single crystal metal surfaces such as supported model catalysts. Its ability to monitor enantiomeric excess in disordered layers of surface intermediates is unique and makes it a highly powerful probe. The technique will widen the range of problems that can be studied, and will hence facilitate improved understanding of chiral adsorbate-metal phenomena and asymmetric surface reactions.

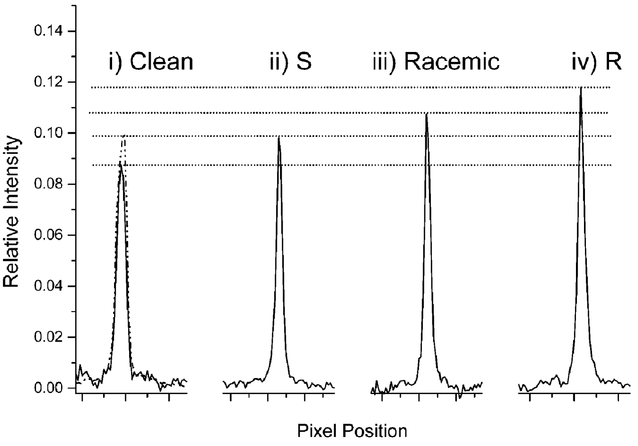

Fig. 1 (i) The signals monitored at 35° (solid line) and −55° (dashed line, ×0.1) for the clean surface, (ii) the 35° signal for a monolayer of *S*-2-butanol; (iii) the 35° signal for a racemic 2-butanol and (iv) the 35° signal for a monolayer of *R*-2-butanol. All the signals have been normalised against their respective −55° signals. Horizontal lines have been added to aid comparison.

Notes and references

1 R. A. Sheldon, *Chirotechnology*, Marcel Dekker, New York 1993.
2 S. M. Barlow and R. Raval, *Surf. Sci. Rep.*, 2003, **50**, 201.
3 G. P. Lopinski, D. J. Moffat, D. D. M. Wayner and R. A. Wolkow, *Nature*, 1998, **392**, 909.
4 M. Böhringer, W. D. Schneider and R. Berndt, *Angew. Chem., Int. Ed. Engl.*, 2000, **39**, 792.
5 M. O. Lorenzo, C. J. Baddeley, C. Muryn and R. Raval, *Nature*, 2000, **404**, 376.
6 J. M. Bonella, F. J. Williams and R. M. Lambert, *J. Am. Chem. Soc.*, 2003, **125**, 2723.
7 S. Sioncke, T. Verbiest and A. Persoons, *Mater. Sci. Eng. Rep.*, 2003, **42**, 115.
8 F. Hache, T. Bolesteix, M. C. Schanne-Klein, M. Alexandre, G. Lemercier and C. Andrand, *J. Phys. Chem. B*, 2003, **107**, 5261.
9 H. W. K. Tom, C. M. Mates, X. D. Zhu, J. E. Crowell, T. F. Heinz, G. Somorjai and Y. R. Shen, *Phys. Rev. Lett.*, 1984, **52**, 348.
10 J. E. Sipe, D. J. Moss and H. M. van Driel, *Phys. Rev. B*, 1987, **35**, 1129.
11 C. F. McFadden, P. S. Cremer and A. J. Gellman, *Langmuir*, 1996, **12**, 2483.