Surface Chemistry

Going Beyond the Physical: Instilling Chirality onto the Electronic Structure of a Metal**

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Conveying chirality onto the electronic structure of a metal surface is a possible mechanism by which chemical reactivity and electrical properties may be made chirally dependent. Here we report for the first time, to the best of our knowledge, that an adsorbed chiral molecule, 1-(1-naphthyl)ethylamine,

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[**] Dr. L. Hecht is thanked for his help with the design of the laser system. A.M., S.M.J., and G.B.D.R. thank the EPSRC for the provision of studentships, and M.K. thanks the EPSRC and the University of Glasgow for funding.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200462265

can reversibly instill chirality onto the electronic structure of a metal surface, a previously unobserved phenomenon. We further demonstrate that although all chiral adsorbates physically convey chirality onto a surface at a local level, not all have the ability to further instill chirality onto the electronic structure of the underlying metal surface. This observation has strong implications for the chiral technologies that are governed by the functionality of these metal surfaces.

On the nanoscale, naturally occurring metal surfaces exhibit planes of mirror symmetry. This mirror symmetry can be lifted and chirality can be "physically" conveyed onto a surface through adsorbtion of a chiral molecule.[1] Metal surfaces that have been functionalized in this way have applications in emerging chiral technologies, such as enantioselective metal-based heterogeneous catalysis, chiral recognition, and sensing.[2] Until now it has been unclear whether the instilling of chirality by an adsorbate is limited to just the physical structure or whether it goes deeper and the electronic structure of the underlying surface can be imbued with chiral character.[3] To establish that the electronic structure of a metal can be reversibly instilled with chirality is highly significant because it offers an alternative view of how chiral adsorbates can induce chiral dependencies in the physical and chemical properties of interfaces. Current understanding of chirally dependent processes is based on purely geometric arguments, and the effects of a "chiral" perturbation on the electronic structure of the interface are not considered.[3]

We investigated single layers of (*R*)- and (*S*)-1-(1-naphthyl)ethylamine (NEA) adsorbed on a Cu(111) surface. NEA was chosen for the study because it has been shown to modify the reactivity of particles of metal catalyst in such a way that they selectively produce a particular enantiomer in hydrogenation reactions.[4] Previous studies of NEA and related cinchona alkaloids on Pt[5] and Cu[6] surfaces have shown that they bind to the surface predominantly through the aromatic ring, which is slightly inclined with respect to the surface. In the case of NEA, the aromatic ring is attached to the asymmetric carbon atom, which also has a methyl group, an amine group, and a hydrogen atom attached to it. In the adsorption geometry adopted by NEA, two of these three groups, as well as the aromatic naphthalene ring, are in close vicinity to the surface (Figure 1).

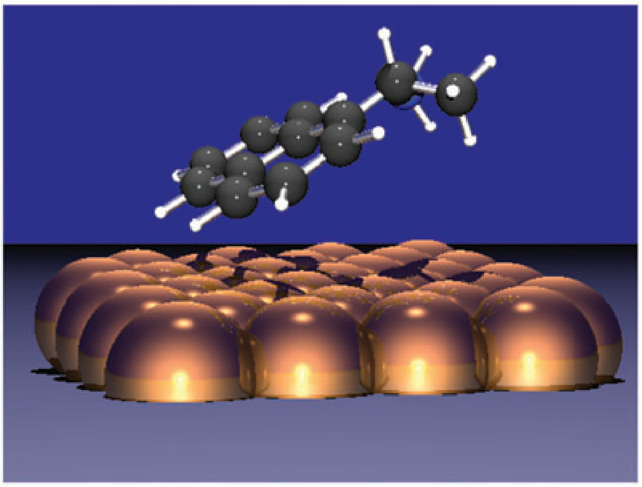

Figure 1. The adsorption geometry of NEA, taken from reference [5], on Cu(111).

NEA interacts weakly with Cu(111) through adsorbtion, without forming strong chemical bonds, and it thermally desorbs from the surface without dissociation below 300 K. The combination of the weak interaction and the cryogenic temperatures at which the layers of NEA are deposited preclude the possibility of the adsorbate inducing chiral restructuring (etching) of the copper surface. Adsorbate-induced chiral restructuring of copper has been observed previously[7] and involves the formation of chiral facets, which have associated chiral electronic states that remain on the surface after the removal of the adsorbate and are stable up to the annealing temperature of the metal (≈ 900 K for Cu).

To determine whether NEA instils chirality onto the surface electronic structure of copper, optically active second-harmonic generation (SHG) measurements are performed; these have been shown to be highly flexible probes of surface chirality.[8] SHG is a nonlinear optical response of an interface which involves the frequency doubling of incident radiation. The SHG response is determined by the second-order susceptibility tensor $\chi^{(2)}$ of the surface. In the optically active variant of SHG that was used in this study, elliptically polarized SHG light (532 nm) was generated from a chiral interface by incident linearly polarized pulsed laser radiation (1064 nm, 8-ns duration). The ellipticity in the SHG light can be viewed as resulting from an optical rotation, the sense of which depends upon the handedness of the chiral interface. Hence the technique can be considered a nonlinear analogue of traditional polarimetry measurements.

The overall $\chi^{(2)}$ value of the NEA/copper interface has two contributions, one from the metal–adsorbate interface ($\chi^{(2)}_{\mathrm{Cu}}$) which is governed by the electronic structure of the metal, and a second from the adsorbate–vacuum interface ($\chi^{(2)}_{\mathrm{NEA}}$). If $\chi^{(2)}_{\mathrm{Cu}} \gg \chi^{(2)}_{\mathrm{NEA}}$, then the SHG signal is only sensitive to the electronic structure of the metal, and an optically active response would be observed only if chirality had been instilled on the surface electronic structure. The $\chi^{(2)}_{\mathrm{NEA}}$ value is governed by the hyperpolarizability (β) of each single molecule, and the number density of surface molecules (N_s). The β value for NEA has not been measured, however, there is considerable experimental data on other monosubstituted aromatic compounds, such as benzenes, stilbenes, and polyphenyls,[9,10] which all display $\beta \leq 10^{-30}$ esu (electrostatic unit). Theoretical work has also shown the polarizability properties of naphthalene are of the same order of magnitude as for benzene.[11] β values of greater than 10^{-28} are only observed in aromatic systems that contain electron-donating and -withdrawing groups: NEA is not of this type. Enhancements of an order of magnitude in $\chi^{(2)}$ values have been reported from chiral films of molecules which have a resonant electronic transition that coincide with the frequency of the second-harmonic (SH) radiation.[12] However, such enhancements are not expected for NEA, which is transparent at the wavelengths of both the incident and SH radiation. This indicates that 10^{-30} esu is an upper limit for the β value of NEA. As a saturated monolayer of NEA has a surface molecule density of approximately

10^{14} cm^{-2},[5] then $\chi^{(2)}_{\mathrm{NEA}} \leq 10^{-16}$ esu, which compares with $\chi^{(2)}_{\mathrm{Cu}} \approx 10^{-12}$ esu.[13]

To further increase the relative contribution that $\chi^{(2)}_{\mathrm{Cu}}$ makes to the overall SH signal, p-polarized (electric field perpendicular to the surface) incident radiation was used. With p-polarized incident radiation the contribution of $\chi^{(2)}_{\mathrm{Cu}}$ to the overall $\chi^{(2)}$ value of the interface is maximized,[14] while the $\chi^{(2)}_{\mathrm{NEA}}$ contribution will be reduced. This reduction in the contribution of $\chi^{(2)}_{\mathrm{NEA}}$ is caused by the fact that the incident electric field is not parallel to the highly polarizable π system of the naphthalene. Given that $\chi^{(2)}_{\mathrm{Cu}} \gg \chi^{(2)}_{\mathrm{NEA}}$, the observation of optical activity in SH measurements will signal the instilling of chirality onto the electronic structure of the metal.

Figure 2 depicts plots of SHG intensity as a function of detection polarization for incident p-polarized light from a clean Cu(111) surface and for overlayers of (*R*)- and (*S*)-NEA (both have identical submonolayer coverages). A symmetrical profile is observed for the clean surface, with maximum intensity observed for p-polarization and minimum intensities for outgoing s-polarization. This behavior is consistent with that expected for an achiral Cu(111) surface. However, there is a dramatic change in profiles for (*R*)- and (*S*)-NEA monolayers. Both are asymmetric about the p-polarization direction, but in the profile for (*R*)-NEA the maximum in SHG intensity peaks close to 45°, while for (*S*)-NEA it is located at −45°. The asymmetry of the two profiles has been parameterized in two ways: the first method uses the ratio I_{45}/I_{-45}, while the second method involves the ratio of the integrated area at negative (I_-) and positive (I_+) angles. All of the measured ratios are listed in Table 1. Both types of ratio show that the profiles for the *R* and *S* isomers are asymmetric and they are those expected for an optically active measurement: I_{45}/I_{-45} for one enantiomer is equal to I_{-45}/I_{45} ratio of the other. SHG polarimetry measurements have also been collected after the NEA layers were removed from the surface through desorption by heating to 273 K. The obtained profiles are once again symmetric about the p-polarization direction.

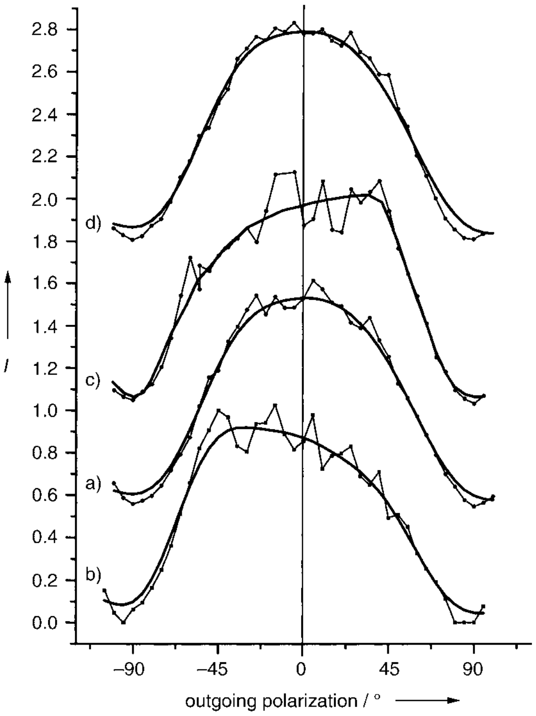

Figure 2. Representative profiles showing second-harmonic (SH, $\lambda = 532$ nm) intensity generated by incident p-polarized laser pulses (duration: 8 ns; wavelength: 1064 nm) from a) a clean Cu(111) surface, b) and c) Cu surface with monolayers of (*S*)- (b) and (*R*)-NEA (c), and d) a surface after the desorption of a monolayer of NEA. The horizontal axis is the detection polarization angle with respect to the p-polarization direction.

Table 1: Parameters showing the asymmetry of SH profiles obtained from monolayers of (*S*)- and (*R*)-NEA.[a]

	I_{45}/I_{-45}	I_{-45}/I_{45}	I_+/I_-	I_-/I_+
(*R*)-NEA	1.50 ± 0.10	0.67 ± 0.07	1.14 ± 0.06	0.88 ± 0.05
(*S*)-NEA	0.75 ± 0.07	$1.33 + 0.13$	0.90 ± 0.06	1.11 ± 0.07

[a] The tabulated values are averages obtained from five freshly prepared surfaces; the quoted errors correspond to one standard deviation in ratios.

The results from SHG polarimetry clearly show that NEA reversibly instills chirality onto the surface electronic structure of Cu(111). The fact that the surface returns to achirality after the desorption of the adsorbate below 300 K rules out, as expected, the possibility of chiral etching by NEA. So, chirality must be instilled onto the surface electronic structure of the metal by the adsorbate without induction of a significant physical chiral rearrangement of the surface itself. The instilling of chirality onto the electronic structure of a metal by an adsorbate is not a generic phenomenon. In previous work,[14] we have found that another chiral molecule, 2-butanol, does not instil the surface electronic structure of Cu(111) with chirality. 2-Butanol, like NEA, interacts weakly with Cu(111) desorbing from the surface below 300 K. We believe that the ability of NEA to instil chirality is associated with its adsorption geometry. NEA adopts a geometry that results in a “chiral footprint”, in which three different chemical groups are in close proximity to the surface. In contrast, 2-butanol does not have a chiral footprint, as it adopts a geometry where only a single group, the hydroxyl, is close to the surface.[15] An analogy can be drawn between our hypothesis and the observed behavior of chiral inorganic metal complexes. The electronic structure of a metal ion that is in a chiral ligand environment has chiral character, which is revealed by the observation of circular dichroism (CD) in UV/Vis absorption bands associated with transitions localized to the metal center. This observation suggests that the chiral footprint plays the same role as the chiral ligand environment and reduces the symmetry of the surface electronic states from C_{3v} to a chiral point group. On the basis of this mechanism, we predict that a prerequisite for the instilling of chirality is an adsorption geometry that displays a chiral footprint on the surface.

The conveyance of chirality onto the surface electronic structure of a metal challenges the established view of the mechanisms by which chiral adsorbates induce enantioselectivity in surface reactions. Current models for the mechanism are based on solely geometric arguments,[16–18] in which the adsorbed chiral modifier interacts with the achiral reactants to control the stereochemistry of the surface transition state and, consequently, of the reaction products. The models can explain some but not all of the features of enantioselective reactions, and in particular they cannot predict in a meaningful way the effect of structural variations of the modifier on enantioselectivity.[19] We suggest that to fully model the action of a chiral modifier, its ability to instill chirality on the surface electronic structure should be taken into account. In the case where a modifier instills chirality onto the electronic structure, the absolute configurations of a chiral transition state and chiral product would be expected to govern how strongly they interact with the metal surface, which will influence directly the thermodynamics of the reaction and consequently enantioselectivity. Similar "chiral" electronic effects on the thermodynamics of the adsorbed state have clear implications for the mechanisms of chiral separation and recognition, which are currently also understood by using solely geometric arguments.[2] In summary, this new insight pushes forward the boundaries of the understanding of chiral adsorption phenomena and consequently should aid in the future development of lucrative chiral technologies.

Experimental Section

For optimal control of the NEA/copper interface, experiments were performed under ultrahigh vacuum (UHV) conditions (base pressure: 1×10^{-10} mbar) using an atomically clean well-ordered Cu(111) single-crystal surface. Single layers of (*R*)- and (*S*)-NEA were deposited from the vapor phase onto Cu(111) at 100 K. SHG measurements were performed using pulses (8–12 ns) of fundamental Nd:YAG laser (Spectra Physics Quanta Ray) 1064-nm radiation at a repetition rate of 10 Hz and around 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 polarization was varied by using a $\lambda/2$ plate. The SH signal was monitored at 60° with respect to the surface normal: it first passed through a polarizer before being focused into a spectrograph and then detected on an intensified CCD camera.

Received: October 11, 2004
Revised: November 2, 2004

Keywords: adsorption · chirality · copper · electronic structure · surface chemistry

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