Wednesday Afternoon, November 12, 2014

Surface Science
Room: 309 - Session SS-WeA

Chirality and Enantioselectivity on Surfaces

Moderator: Melissa A. Hines, Cornell University, Andrew Teplyakov, University of Delaware

2:20pm SS-WeA1 Simple Rules and the Emergence of Chirality at Surfaces, *Rasmita Raval*, University of Liverpool   **INVITED**
Chiral surfaces can be created by the adsorption of intrinsically chiral molecules, with the handedness defined by the molecule [1-4]. Additionally, a second manifestation of chirality may arise due to the molecule-substrate interaction in the form of chiral adsorption footprints. Recent advances have allowed both levels of chirality to be determined at the single-molecule level [5-8] and, surprisingly, reveal a wide range of chiral orderings. How both these aspects unfold and express themselves in organized molecular layers at surfaces is little understood. This talk will illustrate how the emergence of chirality in organised assemblies of amino-acids on a Cu(110) surface can be understood in terms of simple generic rules.

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[2] N. Liu, S. Haq, G. R. Darling and R. Raval, 'Direct Visualisation of Enantiospecific Substitution of Chiral Guest Molecules into Heterochiral Molecular Assemblies at Surfaces' Angewandte Chemie Int.Ed., 46 (2007) 7613.

[3] P. Donovan, A. Robin, M. S. Dyer, M. Persson, R. Raval, 'Unexpected Deformations Induced by Surface Interaction and Chiral Self-Assembly of Co(II)-Tetraphenylporphyrin adsorbed on Cu(110): A combined STM and Periodic DFT study'. Chemistry, A European Journal, 16 (2010) 11641.

[4] S.Haq, N. Liu, V.Humblot. A.P.J.Jansen, R.Raval, 'Drastic Symmetry Breaking in Supramolecular Organization of Enantiomerically Unbalanced Monolayers at Surfaces'. Nature Chemistry, 1 (2009) 409-414.

[5] M. Forster, M. Dyer, M. Persson and R.Raval, 'Probing Conformers and Adsorption Footprints at the Single-Molecule Level in a Highly Organized Amino Acid Assembly of (S)-Proline on Cu(110)'. J. Am. Chem. Soc., 131 (2009) 10173-10181.

[6] M. Forster, M. Dyer, M. Persson and R.Raval, '2-D Random Organization of Racemic Amino-Acid Monolayers Driven by Nanoscale Adsorption Footprints: Proline on Cu(110)', Angewandte Chemie Int. Ed., 2010 (49), 2344-47.

[7] A.G. Mark, M. Forster, R. Raval, Recognition and Ordering at Surfaces: The Importance of Handedness and Footedness. ChemPhysChem 2011, 12, 1474.

[8] M.Forster, M.S. Dyer, M. Persson, R.Raval, Tailoring Homochirality at Surfaces: Going Beyond Molecular Handedness. J. Am. Chem. Soc. 2011, 133, 15992.

3:00pm SS-WeA3 Exploring Enantioselectivity on Chirally Modified Surfaces in Ultrahigh Vacuum, *Wilfred T. Tysoe*, University of Wisconsin-Milwaukee
The mode of operation of heterogeneous chiral modifiers can be classified into those operating as templates, where several modifier molecules act in concert to define a chiral adsorption site, or one-to-one modifiers that form a docking complex between the modifier and a prochiral reactant. Enantioselectivity is measured by adsorbing chiral probe molecules onto chirally modified surfaces. Templating is illustrated using amino acids on Pd(111). Scanning tunneling microscopy (STM) reveals that some amino acids form tetrameric units, and others form dimers. Only those amino acids that form tetramers are enantioselective implying that the tetramers act as templates.

Naphthylethylamine (NEA) is proposed to acts as a one-to-one modifier. The interaction between NEA and a prochiral reactant, methyl pyruvate, is explored using STM. Possible docking complexes are identified using density functional theory and the simulated images are compared with experimental images.

3:20pm SS-WeA4 The Structure Sensitivity of L and D Tartaric Acid Explosive Decomposition on Copper Surface Structure Spread Single Crystals, *Aaron Reinicker*, B.S. Mhatre, B.S. Holsclaw, Carnegie Mellon University, *E.C.H. Sykes*, Tufts University, *A.J. Gellman*, Carnegie Mellon University
There are many catalytic reactions that are sensitive to the surface structure of the catalyst. Surface Structure Spread Single Crystals (S^4Cs) expose a continuous distribution of crystal planes across their surfaces. Each point on the S^4Cs has a different local crystallographic orientation that can be determined from the shape of the S^4Cs and the orientation of its bulk crystal lattice vectors. Crystal planes on these S^4Cs contains terraces, monatomic steps, and kinks and can be described as chiral with an R or an S orientation. When coupled with spatially resolved surface analysis techniques, S^4Cs can be used to study the effects of surface structure and chirality on surface chemistry across a broad, continuous distribution of crystal planes. In this work, the structure sensitivity of L and D tartaric acid explosive decomposition was studied using a Cu(111)±10° S^4C. Isothermal Temperature Programmed Desorption (TPD) was used in which each sample was held at a temperature >20 K below the temperature of peak decomposition observed in a standard (TPD) experiment until the decomposition reaction occurred. Spatially resolved X-ray Photoelectron Spectroscopy (XPS) was performed to determine which crystal planes on the Cu(111)±10° S^4C had undergone explosive decomposition after quenching the temperature of the sample at the decomposition peak during an isothermal TPD. Quenching the sample at different times during the isothermal TPD decomposition peak was implemented to visualize the stages of reaction on the Cu(111)±10° S^4C surface. It was found that both D-tartaric acid and L-tartaric acid reacted on crystal planes with (100) steps before crystal planes with (111) steps and the surface structure had more of an effect on the explosive decomposition of tartaric acid than the surface chirality.

4:20pm SS-WeA7 Ordering of L-alaninate Superstructures on Cu(001), *Erkan Ciftlikli*, B.J. Hinch, Rutgers University
Multiple domains of a c(4x2) superstructure are produced following dissociative L-Alanine adsorption on Cu(001) at temperatures of 0 °C and above. The anticipated structure at 0.25ML relies on stabilization of a tridendate surface species, in ordered arrays, held together with intermolecular H bonding. He atom diffraction is benign, and the films can be investigated over the course of days. The saturated c(4x2) structure is stable up to ~200°C. In contrast the subsaturation surfaces are thermally unstable and a slow relaxation occurs after nucleation of c(4x2) domains. He-surface bound state resonances are seen to affect the symmetries of the He diffraction intensities and the inelastic He-phonon cross sections observed from the chiral adsorbate. The enhanced inelastic scattering intensities are used to compare the vibrational characteristics of saturated and sub-saturation L-Ala/Cu(001) surfaces.

4:40pm SS-WeA8 Quantitation of Enantiospecific Adsorption on Chiral Nanoparticles from Optical Rotation, *Nisha Shukla*, N. Ondeck, N. Khosla, A.J. Gellman, Carnegie Mellon University
Au nanoparticles modified with enantiomerically pure D- or L-cysteine have been shown to serve as enantioselective adsorbents of R- and S-propylene oxide [1]. A simple adsorption model and accompanying experimental protocol have been developed to enable optical rotation measurements to be analyzed for quantitative determination of the ratios of the enantiospecific adsorption equilibrium constants of chiral species on the surfaces of chiral nanoparticles, $(K^S_L / K^S_D) = (K^R_D)/(K^R_L)$. This analysis is robust in the sense that it obviates the need to measure the absolute surface area of the absorbent nanoparticles, a quantity that is somewhat difficult to obtain accurately. This analysis has been applied to optical rotation data obtained from solutions of R- and S-propylene oxide, in varying concentration ratios, with D- and L-cysteine coated Au nanoparticles, in varying concentration ratios [2].

[1] N. Shukla, M.A. Bartel, A.J. Gellman "Enantioselective separation on chiral Au nanoparticles" Journal of the American Chemical Society, 132(25), (2010), 8575–858.

[2] N. Shukla, N. Ondeck, A.J. Gellman "Quantitation of Enantiospecific Adsorption on Chiral Nanoparticles" Surface Science, (accepted-2014).

5:00pm **SS-WeA9 Low-Temperature STM Observation of Asymmetrical Adsorption and Chirality of Ga Adatoms on Wurtzite GaN(000-1)**, *Khan Alam*, A. Foley, J. Corbett, Y. Ma, J. Pak, A.R. Smith, Ohio University

A sample with atomically flat terraces having the c(6×12) reconstruction on GaN(000-1) surface is grown by molecular beam epitaxy and studied at liquid helium temperature using scanning tunneling microscopy. Being the most Ga-rich reconstruction (corresponding to the Ga stability limit) occurring on the N-polar GaN surface,[1] low-temperature STM imaging reveals new details of the c(6×12), although not inconsistent with the early model.[2] Unexpectedly however, a dilute concentration (0.0031 ML) of single atomic adsorbates not seen at room temperature is found covering the terraces. The coverage is stable with time and increases with Ga flux during growth. These adsorbate features are thus attributed to the condensation of Ga adatoms which at room temperature would be in a 2D gas-like state at the surface. Surprisingly, the Ga adsorbates manifest at ~+2.5 V sample bias as distinct L-shapes which are always in one of two possible orientations with respect to <10-10>. Furthermore, on any given atomic terrace, the probability of finding one of the two L-shape orientations is 80%, reversing across a step. However, no in-plane rotation will result in the opposite handed-ness of an L-shape, on either terrace. The L-shaped adsorbates thus reveal broken chiral symmetry linked to adsorption probability, which is attributed to symmetry breaking of the c(6×12) reconstruction.

5:20pm **SS-WeA10 Enantioselectivity and Auto-Amplification by Adsorption**, *Andrew Gellman*, Y. Yun, Carnegie Mellon University

Metal surfaces can be rendered chiral by cleavage along low symmetry planes of the bulk metal lattice. Their chirality results in the enantioselective adsorption of chiral molecules from racemic mixtures. This work has developed and applied a ^{13}C isotopic labeling method for mass spectrometric detection and quantification of enantiospecific adsorption on chiral surfaces. Enantiomerically pure chiral compounds in which one enantiomer is available in an isotopically labelled form allow the design of experiments in which one can expose chiral or achiral surfaces to mixtures of varying enantiomeric excess in the gas phase (ee_g) and then use mass spectrometry to determine enantiomeric excess on the surface (ee_s).

Exposure of a racemic mixture of D-aspartic acid and ^{13}C-L-aspartic acid to the chiral Cu(3,1,17)$^{R\&S}$ surfaces results in the adsorption of a non-racemic monolayer because of the selective adsorption of one enantiomer over the other. ^{13}C-labeling allows mass spectrometry to distinguish the two enantiomers during desorption from the surface.

These measurements have been used to quantify the enantiospecific adsorption equilibrium constants and the enantiospecific difference in the free energies of adsorption of D- and L-aspartic acid on the chiral Cu(3,1,17)$^{R\&S}$ surfaces.

Not surprisingly, exposure of a racemic mixture of D- and ^{13}C-L-aspartic acid to the achiral Cu(111) results in the adsorption of a racemic mixture; in other words, a gas phase mixture with $ee_g = 0$ results in an adsorbed mixture with $ee_g = 0$. However, exposure of the achiral Cu(111) surface to a gas phase mixture with $ee_g = 0.2$ results in an adsorbed phase with $ee_s = 0.4$. In spite of the fact that the surface is achiral adsorption results in auto-amplification of enantiomeric excess. Although the mechanism of auto-amplification has not been confirmed, one can show that this can be a simple consequence of adsorption of gas phase monomers in the form of homochiral clusters L_n or D_n.

In general, during adsorption on chiral surfaces, the phenomena of enantiospecific adsorption and auto-amplification must be occurring and either competing or augmenting one another.

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