

Surface Science

Room: 202 A - Session SS-ThM

Chirality & Enantioselectivity on Surfaces

Moderator: J. Millunchick, University of Michigan

8:20am **SS-ThM2 Creation of Local Chiral Surface Environments via the Adsorption of Propylene Oxide on achiral Pt(111) Surfaces**, S. Karakalos, F. Zaera, University of California, Riverside

The efficient development of enantiomeric separations has become increasingly important, especially in the pharmaceutical industry, as optical isomers often show different biological behavior, some detrimental to physiological functions. Two-dimensional (2D) molecular surface science aims at understanding molecular recognition, the nature and consequences of intermolecular interactions. The identical alignment of molecules due to adsorption on 2D surfaces, imposes a directionality among lateral interactions. In this study, temperature programmed desorption (TPD), molecular beam (MB) experiments, and Monte Carlo (MC) simulations have been carried out to investigate how propylene oxide (PO), a small chiral molecule, can act as a seed to induce enantioselective adsorption on Pt(111) single-crystal surfaces. TPD results showed that the adsorption of a small initial amount of enantiopure PO on Pt(111) leads to differences in the coverages of a second adsorbate such as enantiopure propylene oxide or propylene (Py), as probed by using a third molecule. Additional studies of isotope exchange on the Pt(111) surface by coadsorbing regular and deuterated PO showed significant replacement of the initially adsorbed PO by the incoming molecules. By using deuterated Py with regular PO, it was also possible to assess the contribution of each molecule on the total coverage on the surface and establish that the induced chirality from the seeding PO plays a crucial role in the final surface coverage. The sticking probabilities of Py, measured by MB experiments on clean Pt(111) and on various PO/Pt(111) systems, identified differences in the adsorption kinetics indicating that the adsorbed chiral PO can lead to desired enantioselective reactions. Initial Monte Carlo simulations have shown promise in their ability to reproduce these sticking probabilities.

8:40am **SS-ThM3 Enantiospecific Adsorption and Decomposition of Aspartic Acid on Cu(hkl)^{R&S} Surfaces**, A.J. Gellman, Y. Yun, B.S. Mhatre, Carnegie Mellon University

One of the key experimental challenges in the study of enantioselective surface chemistry is the development of tools or methods that can distinguish one enantiomer from the other. For two reasons we have identified aspartic acid ($\text{HO}_2\text{CCH}(\text{NH}_2)\text{CH}_2\text{CO}_2\text{H}$) as an ideal chiral probe for studying enantioselective surface chemistry on naturally chiral Cu single crystal surfaces. Firstly, it exhibits extremely highly enantiospecific surface reaction rates because of the fact that it decomposes by an explosive mechanism with highly non-linear kinetics. Secondly, it is an amino acid and as a consequence we are able to use *L-aspartic acid-1,4-¹³C₂ (*L-Asp) which can be distinguished from D-aspartic acid (D-Asp) using mass spectrometry. These have been studied on the achiral Cu(110) and chiral Cu(3,1,17)^{R&S} surfaces. Decomposition of Asp on the Cu(110) and chiral Cu(3,1,17)^{R&S} surfaces yields CO₂ and CH₃-C¹³N as primary products. Not surprisingly, ¹³C labeling in *L-aspartic acid-1,4-¹³C₂ show that the ¹³CO₂ comes only from the carboxylate end-groups while labeling of other atoms shows that the CH₃-C¹³N product arises only from the C2 and C3 carbon atoms. Exposure of a racemic mixture of *L-Asp and D-Asp has been used to establish enantiospecific adsorption equilibria on the Cu(3,1,17)^{R&S} surfaces. During exposure to the racemic mixture, the enantiomer with the higher binding energy is capable of displacing the more weakly bound enantiomer to establish a non-racemic adsorbed layer. In other words, exposure of the Cu(3,1,17)^{R&S} surfaces to the racemic mixture in the gas phase results in a separation and enrichment of one of the two enantiomers on the surface. This can be measured quantitatively to determine the ratios of the enantiospecific adsorption equilibrium constants; $K_S^D/K_R^D = K_R^L/K_S^L = 2.29 \pm 0.17$. These translate into an enantiospecific difference in free energies of adsorption of $\Delta\Delta G = 3.15 \pm 0.29$ kJ/mol. This favors adsorption of L-Asp on the Cu(3,1,17)^R surface and D-Asp on the Cu(3,1,17)^S surface. Although the adsorption energetics of D-Asp and *L-Asp on the Cu(3,1,17)^{R&S} surfaces are enantiospecific, the decomposition kinetics are not. However, on the Cu(643)^{R&S} surfaces the decomposition kinetics exhibit extremely high enantioselectivity. This arises from the non-linear kinetics of the explosion decomposition mechanism.

9:00am **SS-ThM4 Imaging a Surface Explosion: Autocatalytic Desorption of Tartaric Acid from Cu(110)**, T.J. Lawton*, Tufts University, B.S. Mhatre, V. Pushkarev, B.S. Holsclaw, A.J. Gellman, Carnegie Mellon University, E.C.H. Sykes, Tufts University

Autocatalytic reactions occur in a variety of fields and are characterized by an initiation event causing the rate of a reaction to increase non-linearly until it ceases. In addition to occurring in ambient environments, this type of reaction has been observed in a growing number of systems on single crystal surfaces (sometimes called surface explosions) under ultra high vacuum conditions but the mechanism for this process has not been fully determined. These well-controlled model surfaces allowed us to study the progression of an autocatalytic reaction, the thermal decomposition of tartaric acid (TA) on a Cu(110) single crystal surface, with molecular resolution imaging using scanning tunneling microscopy (STM) and temperature programmed reaction spectroscopy (TPRS). Using STM we progressively anneal the tartaric acid system and obtain the first molecular-scale images during a surface explosion to determine the changes occurring as a function of temperature. From these images we determine that the density of molecules slightly decreases until a critical threshold is reached when the molecules can decompose then desorb. We also observe, for the first time, a new phase of TA complexed with Cu adatoms that may play a role in the surface explosion as it occurs at the onset of the explosion. One area in which an understanding of autocatalytic reactions could be exploited is the separation of enantiomers from a heterogeneous catalyst. In this example a more complete separation of enantiomers could be achieved compared to normal desorption kinetics.

9:20am **SS-ThM5 Exploring Enantioselectivity on Chirally Modified Surfaces in Ultrahigh Vacuum**, W.T. Tysoe, University of Wisconsin Milwaukee **INVITED**

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 aminoacids on Pd(111). Scanning tunneling microscopy (STM) reveals that some aminoacids form tetrameric units, and others form dimers. Only those aminoacids that form tetramers are enantioselective implying that the tetramers act as templates.

Naphthylethylamine (NEA) is proposed to act 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.

10:40am **SS-ThM9 Spin-dependent Electron Transmission through Helical Organic Molecules**, B. Goehler, M. Kettner, University of Muenster, Germany, T.Z. Markus, R. Naaman, Weizmann Institute of Science, Israel, H. Zacharias, University of Muenster, Germany

Since more than a decade the field of spintronics deals with the manipulation of the electron spin to facilitate electronic operations. For such devices spin-dependent electron transfer processes (namely spin filters) are needed, which are usually realized using either magnetic materials or systems containing heavy atoms to make use of spin-orbit coupling. Here we present spin-selective electron transmission through organic molecules with helical symmetry of quite high filtering efficiencies.

The work is based on "electron dichroism", an effect that describes different interactions of longitudinally spin-polarized electrons with chiral molecules. Experiments in the mid-90s showed that spin-polarized electron beams, guided through vapor of chiral molecules, are attenuated differently, depending on the longitudinal spin polarization of the electrons and the enantiomer of the molecules.

Studying the transmission of low-energy photoelectrons through ordered self-assembled monolayers of chiral molecules on gold, an intensity dichroism was observed between the excitation with circularly polarized light of opposite helicity, which has been interpreted as a spin-dependent transmission through these ordered layers. We extend these studies by directly measuring the electron spin polarization using a calibrated Mott detector [1]. The observed spin selectivity at room temperature is extremely high as compared to other known spin filters. A systematic study on DNA monolayers shows that the spin filtration efficiency depends on the length

* Morton S. Traum Award Finalist

and organization of the adsorbed molecules: single-stranded DNA molecules, which form a rather floppy instead of an ordered layer, show almost no spin-filtering effect. Recently, the spin transmission studies have been extended to bacteriorhodopsin membrane protein physisorbed on gold and aluminum surfaces. Spin polarization measurements yield up to 15% spin polarization for transmitted electron ensembles with a minor dependency on the preparation scheme. Results obtained using an Al substrate yield that the high spin-orbit coupling of the Au substrate used in former experiments does not influence the effect. Because of the low atomic numbers of the constituents (P, C, H) of the organic molecules adsorbed on the surface, spin-orbit-coupling is not sufficient to explain the observation of the quite large spin-specific interaction. Even though very recently different models were published aiming to rationalize the observed effect, it is not understood so far.

[1] Science, 331, 894 (2011)

11:00am **SS-ThM10 Coverage Dependent Self-Assembled Structures of Glutaric Acid on Cu(110)**, *E.H. Park, S. Kim*, KAIST, Republic of Korea

We have investigated the adsorption structure of glutaric acid ($\text{HOOC}(\text{CH}_2)_3\text{COOH}$) on the Cu(110) surface as a function of coverage using Scanning Tunneling Microscopy and Reflection-Absorption IR Spectroscopy. At low coverage, glutaric acid molecules diffuse freely on Cu(110) surface at room temperature, thus they can't form ordered structures at this coverage. However, novel structures have been formed under continuous scanning of the tip. We suggest that this new structures can be created by the field-induced self-assembly. As increasing coverage, glutaric acids are self-assembled by annealing at 450K. At 0.25ML, glutaric acid adsorbs with a bi-glutarate ($-\text{OOC}(\text{CH}_2)_3\text{COO}-$) configuration producing a racemic conglomerate of coexisting mirror domains. Although the molecule is achiral, it forms chiral domains on the surface from adsorption-induced asymmetrization. At 0.5ML, two distinct adsorption configurations are observed which are chiral each other. Overall, the heterochiral structure with chiral chains alternating each other is created at this coverage forming zigzag structure, and still glutaric acid adsorbs with a bi-glutarate configuration. Finally, at 1ML, glutaric acid adsorbs with a mono-glutarate configuration forming close packed structures.

11:20am **SS-ThM11 Enantioselective Decomposition of L and D Tartaric Acid on Copper Surface Structure Spread Single Crystals**, *A. Reinicker, B.S. Mhatre, B.S. Holsclaw, A.J. Gellman*, Carnegie Mellon University

The role of atomic surface structure in catalytic reactions requires a fundamental understanding to develop new catalysts. 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. The majority of 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 chirality on surface chemistry across a broad, continuous distribution of crystal planes. In this work, the enantioselectivity of the explosive decomposition of L and D tartaric acid was studied using $\text{Cu}(100)\pm 10^\circ$, $\text{Cu}(110)\pm 10^\circ$, and $\text{Cu}(111)\pm 10^\circ$ S^4Cs . We used Isothermal Temperature Programmed Desorption (TPD) 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 each S^4C had undergone explosive decomposition after quenching the temperature of each sample at the decomposition peak during an isothermal TPD. It was found that D-tartaric acid decomposes before L-tartaric acid on R oriented surfaces and L-tartaric acid decomposes before D-tartaric acid on S oriented surfaces on all three $\text{Cu S}^4\text{Cs}$.

11:40am **SS-ThM12 Stereodirecting Interactions and Stereodynamics on Chirally Modified Pt(111)**, *Y. Dong, G. Goubert, Y. Zeng, P.H. McBreen, J.-C. Lemay*, Laval University, Canada

The stereocontrol of chemical reactions on surfaces is a challenging task. STM imaging coupled with DFT calculations provides a powerful method for studying asymmetric induction on chirally modified catalysts. In combination, these techniques can be used to observe and define transient pre-organization complexes formed by binding the prochiral substrate to the chemisorbed chiral modifier. We present sub-molecularly resolved regiospecific and stereospecific data for isolated bimolecular and termolecular complexes formed at chiral sites on Pt(111). The measurements provide new insight on both the stereodirecting interactions involved and the dynamics of chiral selection.

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