Surface Science Division
Room 24 - Session SS+HC-FrM
Recent Advances in the Chemistry and Physics of Interfaces

Moderators: Robert Bartynski, Rutgers University, Wei Zhao, University of Washington

8:40am **SS+HC-FrM-2 Enantiospecific Chemistry of Aspartic acid on Copper Surfaces***, **Soham Dutta**,* Carnegie Mellon University*; A Gellman,* Carnegie Mellon University, W.E. Scott Institute for Energy Innovation

Chirality is a geometric property and refers to existence of handedness in any system. While chirality is ubiquitous in nature across all spatial scales, chirality at the molecular level is of special interest given the homochirality of biomolecules such as DNA and the amino acids that are the molecular basis of life. Increasingly, fundamental research is focused on studying chiral molecules adsorbed on surfaces given their applications in enantioselective chemical phenomena such as heterogeneous catalysis. While many examples of 2D chiral assembly of molecules have been studied over the years, fundamental questions about chiral aggregation on surfaces remain unanswered. One such question is whether enantiomers deposited on a surface aggregate into domains containing enantiomers of the same chirality (homochiral) or domains containing both enantiomers (heterochiral).

In this study, we have used a combination of Temperature Programmed Reaction Spectroscopy (TPRS) and isotopic labelling to study the decomposition kinetics and aggregation behavior of aspartic acid (Asp) enantiomers on Cu surfaces. The ionization state of adsorbed Asp monolayer was determined to be anionic using X-ray photoelectron spectroscopy. Next, using isotopic labelling, we have identified Asp decomposition mechanism in greater detail than possible for any comparable size adsorbate on a metal surface. It was found that Asp follows a multi-step decomposition process to form CO_2 and acetonitrile. Then, the first observed enantiospecific decomposition of Asp enantiomers is reported on naturally chiral $Cu(643)^{R\&S}$. Lastly, equilibrium adsorption experiments of Asp enantiomer mixtures on copper surfaces were performed and Asp enantiomers was found to aggregate on the surface. A cluster-adsorption model was developed to quantify the free energy change and equilibrium constants of enantiomer aggregation in 2D for the first time.

The combination of a surface explosion pathway with a naturally chiral catalytic surface leads to high enantiospecificity of Asp decomposition. This non-linear explosive decomposition pathway, coupled with the availability of multiple isotopomers is exploited to quantitatively probe aggregation behavior of aspartic acid with unprecedented detail.

9:00am **SS+HC-FrM-3 Anchoring Carbon Nanotubes to Solid Supports via Direct Attachment Through the Cage***, **Mackenzie Williams**[1], F Gao,* University of Delaware*; I Ben Dhiab,* Université Pierre et Marie Curie*; A Teplyakov,* University of Delaware

The unique physical, optical, and electronic properties of carbon nanotubes (CNTs) have resulted in their integration into devices for a myriad of applications. For this reason, a great number of studies have focused on the many existing methods of chemical attachment of these structures to various support materials. Carbon nanotubes are typically anchored onto these substrates through additional functional groups, such as carboxylic acids, that are present on the CNT edge or defect sites. This typically results in vertical orientation of the CNTs on the surface and the extra linkages of these functional groups may affect the electronic transfer processes through the structure. This may be desired in some cases; however in others, it is preferable to increase the surface contact between CNT and substrate or to preserve the original electronic structure of the CNTs. To this end, we have focused our efforts on direct attachment of CNTs to surfaces. The work described here finds that these extra functional groups on the CNTs are not the only way through which CNTs can bind covalently to a substrate. In fact, the presence of functional groups is not necessary at all for covalent attachment to the surface to occur. Carbon nanotubes containing no additional functional groups were attached to amine-modified gold and silicon substrates directly through the cage structure, similarly to direct attachment that has been found to occur through other caged structures such as C_{60} buckyballs. Microscopy techniques were used to confirm the presence of CNTs in intimate contact with the surface and X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry were used to investigate the chemistry involved. Through comparison to multiple controls, including carboxylic acid-modified CNTs, it was determined that covalent attachment can occur directly through the cage of the CNT. Density functional theory computational methods were used to predict core level binding energies and to confirm the feasibility of this process.

9:20am **SS+HC-FrM-4 Studying Trends in Aromatic Adsorption on Fe{110} using Density Functional Theory Calculations***, **Bianca Provost**,* University of Cambridge, UK*; M Ho, T Hughes,* Schlumberger Gould Research, UK*; J Goodman, S Jenkins,* University of Cambridge, UK

Aromatic adsorption on metal surfaces plays a key role in many fields including heterogeneous catalysis, electrochemical devices, photovoltaics, corrosion protection and chemical sensing. Benzene and to a lesser extent larger aromatic systems have been studied on a variety of metal surfaces both computationally and experimentally.[1-3] However, one metal surface which has received very little attention for aromatic adsorption is iron. Experimental UHV adsorption studies carried out on iron surfaces are complicated by the metal's reactivity and strong tendency to passivate, which result in significant difficulty obtaining a high purity metal surface. Still, iron is deserving of study as it is the major component of steel and catalyses important industrial reactions such as the Fischer-Tropsch and Haber processes. A computational study of the surface chemistry of aromatic molecules on iron will provide novel insight on these systems as well as a level of detail which would not be afforded using experimental techniques.

We have carried out a density functional theory (DFT) study of benzene, naphthalene and quinolinium adsorption on the most stable and therefore predominantly exposed surface facet of a bcc iron crystal, Fe{110}. All identified stable adsorption sites are presented and the most energetically favourable sites are compared across all three studied adsorbate-surface systems. To support the energetic and geometric results of our study, charge density differences, residual spin densities, density of states (DOS) and work function changes have also been calculated and analysed. Finally, we have studied the effect of van der Waals corrected DFT on binding site energetics and geometries. Such corrections have been shown to provide results in better agreement with experiment for aromatic adsorption on certain metal surfaces.[1]

[1] Carrasco, J., Liu, W., Michaelides, A., Tkatchenko, A. *J. Chem. Phys.* **2014**, 140, 084704

[2] Jenkins, S. J. *Proc. R. Soc. A* **2009**, 465(2110), 2949-2976

[3] Netzer, F. P. *Langmuir* **1991**, 7(11), 2544-2547

9:40am **SS+HC-FrM-5 Surface Heterogeneity and Inhomogeneous Broadening of Vibrational Line Profiles***, S Taj, D Baird, A Rosu-Finsen, **Martin McCoustra**,* Heriot-Watt University, UK

The surface heterogeneity of amorphous silica (aSiO2) has been probed using coverage dependent temperature programmed desorption (TPD) of a simple probe molecule, carbon monoxide (CO). As a proof-of-principle, the resulting distribution of interaction energies is the foundation from which an environmentally broadened vibrational line profile synthesis has been undertaken. These simulations are compared with measured line profiles recorded at 0.1 $cm^{-}1$ resolution using reflection–absorption infrared spectroscopy (RAIRS). Additional demonstrations of this methodology on solid water and methanol surfaces will be reported.

10:20am **SS+HC-FrM-7 Ab-Initio Study of Low Index Surface Planes of γ-Al2O3 and their Interface with Pt**, ***Kofi Oware Sarfo**, A Clauser, Z McClure, M Santala,* Oregon State University*; L Árnadóttir,* Oregon State University

Metal/metal oxide interfaces are important because of their substantial impact on the composite properties of materials in a vast range of scientific and technological applications. Historically, metal oxides have been used as thermal barriers to protect metals from thermal degeneration in high temperature environments. Metal/oxide interfaces are important in applications such as protective coatings for metal medical implants, in electronic devices, and in heterogeneous catalysis mostly as catalyst support. γ-Al2O3 is a common catalyst support due to its high surface area, which enables fine dispersal of metal catalysts, such as Pt, Pd, Ru, and Rh. The structure and metal/metal oxide interactions at the interface of these materials can significantly impact the electronic and mechanical properties of the catalyst and the support. In this work, we combine theoretical and experimental approaches to study the nature of the metal/metal oxide interface between γ-Al2O3 and Pt. The theoretical approach utilized density functional theory (DFT) to study the structure and atomistic

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[1] **National Student Award Finalist**

interactions at the interface. To determine the effect of the environment on the stability of different surface termination, we calculate the surface energy of three different low index planes and possible terminations of γ-Al2O3 as a function of partial pressures of oxygen at the experimental fabrication temperature (1100K). The (100) surface plane of γ-Al2O3 was found to be most stable and the (111) surface plane had the highest surface energy corresponding to lowest stability due to its highly polar structure. The stoichiometric terminations were found to be the most stable for the (100) and (110) planes at all partial pressures of oxygen, while the most stable termination of the (111) plane transitions from the stoichiometric surface to an oxygen rich surface termination at higher partial pressures of oxygen. This provides the basis for the experimental study of the atomic structure of the interface between γ-Al2O3 and Pt nanoparticles.

11:00am **SS+HC-FrM-9 Ambient STM Study of Sequentially Adsorbed Octanethiol and Biphenylthiol Monolayers on Au(111)***, **Gaby Avila-Bront**,* College of the Holy Cross

The mixed monolayers of biphenyl-4-thiol (BPT) and octanethiol (OT) are studied at the molecular level using

scanning tunneling microscopy (STM) in ambient conditions and X-ray photoelectron spectroscopy (XPS) on

Au(111). The effect of both the sequence of deposition, and the concentration of the BPT solution used is

investigated. We observe signs of coexisting domains in the form of disordered patches surrounding flat patches

when a 100 µM solution of BPT is used. This observation holds for both OT being deposited first, and BPT being

deposited first. The most clear formation of coexisting domains occurs when an OT monolayer is immersed in a

100 µM solution of BPT. The XP spectra reveal a shift in the C 1s signal of the monolayers that is unique to what

films are deposited on the surface. These data demonstrate the importance characterizing mixed self-assembled

monolayers that form final monolayer structures unique to each mixture.

11:20am **SS+HC-FrM-10 Molecule Assembly Structure and Tilt Geometry Evaluation of 5,6,7-Trithiapentacene-13-one (TTPO) / Pentacene-Quinone on Au(111) with NC-AFM***, A Larson,* University of New Hampshire*; P Zahl,* Brookhaven National Laboratory*; **Karsten Pohl**,* University of New Hampshire

Using non-contact atomic force microscopy (NC-AFM) the 3D molecular structure, tilt and assembly details of a new pentacene-based organic semiconductor, 5,6,7-trithiapentacene-13-one (TTPO) adsorbed on Au(111) were determined. 3D AFM force maps of individually resolved molecular orbitals were acquired to visualize the complete adsorption structure.

Robust, thermally stable, and highly inert to photo-oxidation, TTPO is a very promising organic semiconductor. Simple to synthesize and purify, TTPO readily crystallizes and is indefinitely stable against degradation in acid-free solution. TTPO has a high molar absorptivity, optical and electrochemical HOMO−LUMO gaps of 1.90 and 1.71 eV, respectively. Melting in air from 386−388°C without decomposition, TTPO can be thermally evaporated to produce highly uniform thin films. TTPO has the potential to be used in thin-film electronic devices that require operation over a wide range of temperatures such as transistors, switches, sensors, and solar cells. When adsorbed on a gold electrode, initial scanning tunneling microscopy (STM) experiments and first-principle computation reveal a novel 3-D angular assembly of the TTPO molecules, with the long axis of the molecule parallel to the gold surface, distinctive from any previously observed pentacene and pentacene derivative assemblies. Structures assembled are angularly dependent on TTPO molecular interactions, while commensurate with the underlying gold substrate, allowing for potential tailoring of pi-molecular orbital overlap through tilt-angle control. Understanding of the structure of these novel organic-metallic interfaces will guide nanoscale modifications for improved electrical transport and energy-conversion efficiency in future devices.

Single molecule STM images are input for DFT calculations to model the most-probable adsorption structure, in particular the molecular tilt-angle. NC-AFM, in contrast, is potentially the only technique capable of directly resolving the 3D angular arrangement of the individual adsorbed molecule. Indeed, by evaluating consecutively acquired constant height force maps, we were able to directly measure the 3D structure and tilt of small TTPO and Pentacene-Quinone byproduct assemblies on Au (111). Using GXSM-3, a new constant height mode "fuzzy-regulation" with current based compliance setting was used to scan a wider range of height's otherwise not possible without losing the CO terminated tip molecule. Comparing 3D AFM force maps with a mechanical probe particle based simulation the molecule tilt was evaluated to 11±1°.

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