Monday Afternoon, October 29, 2012

Surface Science
Room: 21 - Session SS-MoA

Surface Dynamics

Moderator: D.J. Auerbach, University of California, Santa Barbara

2:00pm **SS-MoA1 Creation and Reaction of Solvated Electrons at the Vacuum-Liquid Interface**, *W.A. Alexander,* Montana State University, *J.P. Wiens,* University of Wisconsin-Madison, *T.K. Minton,* Montana State University, ***G.M. Nathanson***, University of Wisconsin-Madison **INVITED**
Over the last 70 years, thousands of reactions between solvated electrons and dissolved species have been investigated in water and other protic solvents. Electrons born at the surface of the solvent, however, may react differently than those created within it. In this talk, I will describe gas-liquid scattering experiments using an impinging beam of sodium atoms that ionize upon contact and create electrons at the surface of liquid glycerol. We find that these electrons produce hydrogen atoms and hydrogen molecules, hydroxide ions and water, and glycerol radicals. Remarkably, nearly half the hydrogen atoms created near the surface escape into vacuum before reacting with the solvent .

2:40pm **SS-MoA3 Liquid-Crystal to Solid-Crystal Phase Transition in Flexible Aryl-Triazole Oligomer Adsorbates at the Liquid / HOPG Interface**, ***B. Hirsch***, *K. McDonald, A. Flood, S.L. Tait*, Indiana University - Bloomington
Supramolecular self-assembly at the liquid / solid interface is a powerful strategy for the bottom-up fabrication of complex and well-ordered structures. In order to achieve greater functionality, molecules with functional groups that possess symmetries other than those of the substrate must be included. Here, we explored this idea by integrating the pseudo-C5 triazole moiety into an oligomer through facile synthesis using well-known click chemistry. The molecules initially adsorbed without direct commensuration with HOPG (high oriented pyrolytic graphite) in a lamellar-like liquid-crystalline phase. Subsequent molecular conformational changes are believed to enable a spontaneous phase transition to a more condensed crystalline phase. The crystalline phase forms a dynamic bilayer , in which ripening of the second layer domains was observed. We will present scanning tunneling microscopy (STM) snapshots of this evolution and discuss the dynamics associated with these phase transitions and bilayer formation. Packing models and phase dependence on experimental conditions will be presented. This work lays the foundation for extending the library of self-assembling molecules to develop higher functionality at surfaces.

3:00pm **SS-MoA4 State-Resolved Studies of Methane Activation: Mechanistic Insights into Gas-Surface Reactivity**, ***A.L. Utz***, Tufts University
Gas-surface reactivity measurements performed with vibrational and rotational state selected reagents provide precise energetic resolution that can be exploited to uncover important aspects of gas-surface reactivity. This talk will focus on two examples. In the first, we explore the surface temperature dependent reactivity of methane (CH_4) molecules prepared in the v_3 C-H stretching state. We find that at low incident kinetic energy, thermal excitation of the Ni(111) surface can increase reaction probability by nearly three orders of magnitude. Calculations from the Jackson group provide insight into the origin of this effect. As a second example, we will describe recent experiments that compare the reactivity of the symmetric (v_1) and antisymmetric (v_6) C-H stretching states in di-deutero methane, CH_2D_2, on Ni(111). That work explores how the vibrational symmetry of the reactant molecule may influence the rate and pathway of rapid intramolecular vibrational energy redistribution (IVR) that occurs just prior to reaction, and it tests whether vibrationally adiabatic models for methane activation in the gas phase are also applicable to methane reactivity on a metal surface.

Taken together, the work highlights how general patterns of energy flow within the gas-surface reaction complex can influence reactivity patterns, and how the kinetics of energy redistribution might be used to control or enhance the rate or selectivity of reactions on surfaces.

3:40pm **SS-MoA6 Autocatalytic Decomposition Mechanism of Aspartic Acid on Cu(110) Surfaces**, ***B.S. Mhatre***, *A.J. Gellman*, Carnegie Mellon University
Surface explosions are surface reaction mechanisms wherein an autocatalytic increase in the reaction rate results in the reaction proceeding to completion over a very narrow temperature range during heating. While several substrate-adsorbate systems exhibiting decomposition via surface explosion mechanism have been identified, a detailed understanding of the mechanism remains unclear. We have successfully identified aspartic acid as a suitable probe for studying surface explosion mechanism on Cu(110) surface. Because a wide range of isotopically labeled varieties of aspartic acid are commercially available, we have been able to conduct a detailed investigation of its autocatalytic reaction mechanism. Using specifically labeled aspartic acid molecules, we have identified the reaction products and identified the origins of atoms in the decomposing aspartic acid molecules. The explosive nature of the reaction mechanism has enabled us to study its kinetics using isothermal methods by heating the Cu(110) surface to a constant temperature and then monitoring the product desorption as a function of time. We observe a significant lag time during which nucleation of the reaction is occurring without observable desorption of products. Once the reaction begins, it proceeds to completion over a relatively short time period. Our preliminary studies on chiral Cu(643)$^{R\&S}$ surfaces indicate that aspartic acid exhibits enantiospecific surface decomposition kinetics. The ultimate objective of this work is to be able to identify the mechanism and in particular, the steps in the mechanism which are responsible for the enantiospecificity.

4:00pm **SS-MoA7 Quantum Tunneling Driven Assembly and Diffusion of Hydrogen and Deuterium on Cu(111)**, ***A.D. Jewell****, Tufts University, *G. Peng*, University of Wisconsin Madison, *G. Kyriakou*, Tufts University, *M. Mavrikakis*, University of Wisconsin Madison, *C.H. Sykes*, Tufts University
Hydrogenation reactions are central to the petrochemical, fine chemical, pharmaceutical, and food industries and are of increasing interest in energy production and storage technologies . The processes of molecular adsorption, dissociation, diffusion, association, and desorption are important surface phenomena in heterogeneous catalysis. Typical heterogeneous catalysts often employ alloys based on platinum, palladium, rhodium and ruthenium. While these metals are active at modest temperature and pressure, they are not always 100% selective and are expensive.

Given that molecular hydrogen (H2) dissociation is often the rate limiting step, one strategy is to engineer the minimal catalytic ensemble that will activate H2 but leave the other reactants untouched. We describe a system which offers low dissociation barriers at one location on the surface and weaker binding in other regions. The Pd/Cu surface alloy was prepared in the dilute limit in which 1% Pd resides as individual, isolated substitutional atoms in a 99% Cu(111) surface. In terms of adsorption, these Pd atoms significantly lower the barrier to H2 dissociation and allow the spillover of H atoms onto the Cu surface.[1]

This system also offers the opportunity to study the diffusion, association, and assembly of large quantities of H and D on the Cu(111) surface. Through careful low-temperature scanning tunneling microscopy (STM) tracking experiments we show that quantum tunneling effects dominate the diffusion properties of H and D on the Cu surface.[2] With this direct visualization and quantification of quantum tunneling effects in adatom diffusion, we reveal two types of weak interactions between H adatoms, which lead to assembly into small clusters and larger assemblies of small clusters. We show that the self-assembly of H into large islands is, in fact, a tunneling effect resulting from inter-atom energy being much smaller than the diffusion barrier. We further demonstrate that these latter effects are not at play for D. Density Functional Theory (DFT) calculations provide estimates for both diffusion and interaction energies. Theory also provides quantum tunneling probabilities that agree well with experiment.[2]

References:

[1] G. Kyriakou, M.B. Boucher, A.D.Jewell, E.A. Lewis, T.J. Lawton, A.E. Baber, H.L. Tierney, M. Flytzani-Stephanopoulos, and E.C.H. Sykes, Science **335**, 1209 (2012).

* Morton S. Traum Award Finalist

[2] A.D. Jewell, G. Peng, G. Kyriakou, M. Mavrikakis, E.C.H. Sykes, in preparation.

4:20pm SS-MoA8 H Absorption Depth Profiling Measurement at Ultra-thin Pd(111) Film by Thermal Desorption Spectroscopy, *Y. Aoki, S. Nakajima, H. Hirayama*, Tokyo Institute of Technology, Japan

Palladium is a peculiar metal with non-activated dissociation and bulk incorporation of hydrogen. Previous studies of H thermal desorption spectroscopy (TDS) at Pd(111) indicated that large H_2 exposures at ~100K induce a non-saturating desorption signal which is so called as α peak at 180 K [1]. The absorption origin of the α peak was inferred as the hydrogen located in subsurface sites just below the top surface Pd atoms layer, where it is stabilized at low temperatures by an energy barrier with respect to bulk sites. However, a hydrogen depth profiling measurement by nuclear reaction analysis (NRA) at the Pd(001) surface indicated that the α_1 peak (which regards as α peak at the Pd(111)) has to be assigned to the deeper located H in the 0-50 monolayer [ML] subsurface region [2]. The actual H depth distribution however was difficult to assess precisely with NRA, since the beam induced local heating was suspected to cause a partial escape of H from detection by diffusion into the bulk. To investigate the α-H origin without any heating ambiguity, TDS has been observed at well-defined ultra-thin Pd(111) films. Controlling the Pd film thickness enables us to seek the α-H depth profiling.

Pd film was deposited at the 50 ML of Ag(111) coated Si(111) surface by a Knudsen cell at room temperature. The Pd surface structure was characterized by a reflection high-energy electron diffracion (RHEED) and an atomic force microscopy (AFM). Pd(111) film grew layer-by-layer at the Ag(111) surface when grown at room temperature without any interdiffusion. The lattice constant mismatch between Pd and Ag of 4.9 % expanded the Pd lattice constant when the Pd thickness (θ_{Pd}) was below 80 ML. It recovered the bulk lattice constant at $\theta_{Pd} > 80$ ML. H_2 was exposed to the Pd(111) surface at 102 K with an exposure pressure of 1×10^{-4} Pa. By integrating α-TDS signal, α-H absorption amount of H_2 exposure dependence ($<4\times10^4$ L) and of θ_{Pd} dependence (<560 ML) were observed.

H absorption on the Pd film ($\theta_{Pd}=420$ ML) saturated as ~8 ML at the maximum exposure of 4×10^4 L. The averaged α-H concentration corresponded to 1.9 %. The θ_{Pd} dependence of α-H at the exposure of 4050 L showed that the α-H absorption increased with θ_{Pd} (maximum θ_{Pd} was 560 ML). H concentration at $\theta_{Pd}=80$ ML was 1.8 % which was close to the saturated concentration, it decreased to 1.2 % at $\theta_{Pd}=560$ ML. Our result indicated that the α-H absorption progress from near the surface region, but it possibly to absorb at the deeper bulk region than that of the previous NRA measurement at the high exposures.

References;

[1]. G. E. Gdowski *et al*. Surf. Sci. 181, L147 (1987).

[2]. M. Wilde *et al*. Surf. Sci. 482, 346 (2001).

4:40pm SS-MoA9 Novel Insight Into the Formation Mechanism of Subsurface Hydrogen at Pd(110) Surfaces, *S. Ohno, M. Wilde, K. Fukutani*, The University of Tokyo, Japan

The present study investigates the microscopic hydrogen (H) absorption mechanism at palladium (Pd) (110) single crystal surfaces. The unique properties of H-Pd interactions such as non-activated H_2 dissociation and facile bulk absorption are well known, yet an accurate atomic-level understanding of the H transportation across the surface, i.e., penetration into the Pd interior and hydride formation during absorption as well as the H release into the gas phase has not been achieved. We apply $^1H(^{15}N,\alpha\gamma)^{12}C$ resonant nuclear reaction analysis (NRA) for nondestructive H depth profiling in combination with thermal desorption spectroscopy (TDS) to quantitatively reveal the H-concentration-depth distribution and to unambiguously assign characteristic TDS features to surface-adsorbed and subsurface-absorbed H-species. To obtain additional insight into the release mechanism during thermal desorption of the H states absorbed in the Pd interior, the internal state distribution of desorbing H_2 molecules is characterized with a rovibrational state selective resonance-enhanced multi-photon ionization (REMPI) technique.

TDS experiments using isotope labeling for the surface-adsorbed and subsurface-absorbed H states reveal that two parallel absorption routes exist that lead to two distinctly different depth distributions of Pd hydride in the near-surface region which give rise to separate TDS signatures (α_1 at T=160 K and α_3 at T>190 K), respectively. The first absorption pathway involves only a few (~4%) minority sites (presumably defects) at which penetration is highly efficient and leads to in-plane localized nucleation of hydride that remains concentrated within a few nanometers below the surface (α_1 state). The second absorption route proceeds on regular terraces with a significantly slower penetration rate per site so that subsurface H diffusion leads to a more extended hydride depth distribution (α_3 state, several tens of nm below the surface). A clear difference between the two H absorption

states (α_1, α_3) is also seen in the REMPI internal-state populations of desorbing H_2. Both absorption pathways critically require gas phase H_2, replace surface-adsorbed H atoms with the gas phase isotope, and have activation energies (< 100 meV) much smaller than expected for the isolated subsurface migration of chemisorbed H. The results are accounted for by a concerted mechanism, in which pre-adsorbed H transits into the subsurface while its vacated adsorption site is simultaneously refilled by a nearby 'nascent' H atom in a state of high potential energy, which is supplied through gas phase H_2 dissociation at vacancies in the chemisorption layer.

5:00pm SS-MoA10 Glide-Plane-Specific Selectivity of HREELS Demonstrated in H:Si(110)-(1x1) Phonon Dispersion, *T. Yamada*, RIKEN, Japan, *S.Y. Matsushita*, Tohoku University, Japan, *H. Kato*, Science University of Tokyo, Japan, *A. Kasuya, S. Suto*, Tohoku University, Japan

We observed the consequence of surface glide-plane symmetry over the phonon vibration on a typical, well-defined silicon wafer. We recorded surface phonon dispersion curves on hydrogen-terminated Si(110)-(1×1) by means of high-resolution electron energy loss spectroscopy (HREELS). This surface, H:Si(110)-(1×1), was prepared by etching a Si(110) wafer in 40% aqueous solution of NH4F. H:Si(110)-(1×1) structure involves a glide-plane symmetry, denoted as *p2mg*, along the short segment of the rectangular unit cell, containing two H-Si bonds. This glide-plane symmetry is also lucid in the extinction rule observed in the pattern of low energy electron diffraction (LEED). The normal vibrational modes are doubled into the in-phase and anti-phase modes. However, for the phonons propagating along the glide plane, ones of those pairs are excluded according to the wave vector. The H-Si symmetric stretching, anti-phase out-of-plane bending, and anti-phase in-plane bending exist only for the wave vectors in the 1st Brillouin zone, and the others exist only in the 2nd Brillouin zone. The impact scattering selection rule furthermore limits the normal modes visible to HREELS.We have verified this special case of phonon dispersion by recording angular-resolved vibrational spectra. The surface phonon dispersion curves were recorded over the 1st and 2nd Brillouin zones, by adjusting the angular configuration as well as the incident electron energy. The experimental dispersion curves are in a fair agreement with the theoretical prediction [2]. However, along Γ-X direction, the H-Si stretching mode (~2080 cm$^{-1)}$ just composes a single branch as a concatenation of the symmetric mode in the 1st Brillouin zone, and the asymmetric mode in the 2nd Brillouin zone. Similarly, the out-of-plane bending (~680 cm^{-1}) curve is also single. This is due to the glide-plane symmetry. The in-plane bending modes are all cancelled by the EELS impact selection rule. As for the propagating direction vertical to the glide plane (Γ-X' direction), the pairs of stretching and out-of-plane bending appear simultaneously. The sub-surface phonon modes (< 600 cm^{-1}) also follow the same rule. This is a special case for the glide-plane symmetry, reflected over the reciprocal unit cell as the property of phonon waves propagating along the surface.[1] M. Eremtchenko et al., Surf. Sci. 582 (2005) 159.[2] V. Gräschus et al., Phys. Rev. B 56 (1997) 6482.

Authors Index
Bold page numbers indicate the presenter