

Tuesday Afternoon, October 21, 2008

Surface Science

Room: 209 - Session SS2-TuA

Dynamics and Novel Probes

Moderator: M.G. White, Brookhaven National Laboratory and State University of New York at Stony Brook

1:40pm **SS2-TuA1 Excited Electrons in Interfacial Chemistry**, *A.M. Wodtke, I. Rahinov, R. Cooper*, University of California, Santa Barbara, *D.J. Auerbach*, GRT Inc. **INVITED**

Developing a predictive understanding of surface reactivity incorporating the possible breakdown of the Born-Oppenheimer approximation represents one of the most important challenges to current research in chemical dynamics. Furthermore, to the extent that Born-Oppenheimer breaks down, we have no predictive theory of surface chemistry. This means we are working in an exciting environment where new phenomena might be discovered through experiments and inspire new theoretical developments. This lecture will present recent experimental results from our group that bears on this topic. For example, when molecules with low levels of vibrational excitation collide with metal surfaces, vibrational coupling to electron-hole pairs is not found to be strong unless incidence energies are high. However, there is accumulating evidence that coupling of large amplitude molecular vibration to metallic-electron degrees-of-freedom can be strong and becomes more important at reduced incidence translational energies. This can occur due to charge transfer between the surface and the molecule and the high kinetic energies associated with bond compression/formation. These conditions found in these experiments simulate reaching a chemical transition-state also and we are intrigued to pose the basic question: are electronically non-adiabatic couplings important at transition-states of reactions at metal surfaces? This implies theoretical approaches relying on the Born-Oppenheimer approximation may not accurately reflect the nature of transition-state traversal in reactions at metal surfaces. In related work, we have been looking at the energy transfer processes between molecules and surfaces that enable molecular trapping, the first elementary step in "Langmuir-Hinshelwood" reactions. We find remarkably large amounts of translational energy can be channeled to a metal surface and are able to look at this for different quantum-state to state scattering channels. While our results require additional theoretical comparisons, it appears that phonon coupling may not be sufficient to explain these experimental observations.

2:20pm **SS2-TuA3 Chemicurrent Measurements using Alkali Metal Covered Pd/p-Si(001) Schottky Diodes**, *D. Krix, K. Huba, H. Nienhaus*, University of Duisburg-Essen, Germany

Non-adiabatic energy dissipation, e.g. the creation of electron-hole pairs, plays an important role in the understanding of chemical reactions at metal surfaces. For a large number of gas-metal reactions it is possible to measure hot charge carriers produced while exposing the metal to reactive gases as chemicurrents. The method is based on depositing thin metal films on a semiconducting substrate in order to form a rectifying electrical device - i.e. Schottky diodes. Hot electrons and holes may be ballistically injected into the semiconductor for energies larger than the intrinsic barrier at the interface. Thermalising in the bulk of the semiconductor the current can not flow back into the metal other than through the measuring circuit. Therefore large area, nanometer thick Pd films were grown on wet chemically prepared, hydrogen terminated, Boron doped p-Si(001) substrates. The palladium diodes are used as a platform for further deposition of alkali metal layers. Palladium was chosen for its low barrier height (0.38 eV) on p-doped silicon, making the diodes most sensitive to low energetic hot holes while retaining excellent device characteristics. This barrier is also considerably lower than that of pure alkali-Si diodes - 0.58 eV for potassium. Chemicurrent, Auger spectroscopy, as well as Kelvin probe data are presented for the adsorption of molecular oxygen and molecular hydrogen on Pd and K/Pd surfaces at low temperatures ($T = 120$ K). During the oxidation with molecular oxygen the chemicurrents show as at least two distinct maxima. Varying the initial alkali coverage changes the relative contribution of the maxima to the chemicurrent. The overall charge detected increases monotonically with potassium coverage. After the deposition of about two monolayers of potassium a saturation is seen of about $1\mu\text{As}/\text{cm}^2$. Increasing the Pd film thickness results in a strong exponential attenuation of the observed charge. This is strong support for the identification of the detected currents as due to hot hole generation at the surface. The data give an estimate of the probability to generate a hot hole in a reaction event of approximately 1%.

2:40pm **SS2-TuA4 The Role of Surface Atom Motion in Methane Activation on Ni(111)**, *V.L. Campbell*, Tufts University, *D.R. Killelea*, University of Chicago, *N. Chen, A.L. Utz*, Tufts University

Quantum state resolved gas-surface reactivity measurements have yielded detailed insights into how a gas phase reagent's vibrational energy promotes reaction, but our understanding of how surface vibrations influence reactivity is less complete. Here, we show that state-selected reagents, with their precisely defined internal and translational energy, are powerful probes of the reaction dynamics along other important energetic degrees of freedom, including surface atom motion. We focus on how surface atom motion influences the distribution of energetic barriers experienced by methane molecules prepared in $v=1, J=2$ of the v_3 C-H stretching state and incident on a clean Ni(111) surface. Recent theoretical work suggests when a nickel atom is displaced above the (111) surface plane, the energetic barrier for reaction decreases. Within a dynamical framework, this result suggests that increasing surface temperature increases the probability that an incident methane molecule will impact on a Ni atom in this energetically favorable geometry. Statistical models of reactivity assume that energy in phonon modes is pooled to activate the reaction complex; increased surface temperature increases the pool of energy available to activate the reaction. We use state-selected reagents, with their well-defined internal and translational energies, to quantify reaction probability as a function of incident kinetic energy at a series of surface temperatures. At each surface temperature, the state-resolved reaction probability curves we obtain reveal the effective distribution of barriers along the translational energy coordinate. Changes in the shape of the effective barrier height distribution function with respect to surface temperature reveal how surface atom motion impacts reaction energetics. Our ability to prepare and control the non-equilibrium distribution of energy among the many degrees of freedom in this system permits a test of the energy pooling assumption.

3:00pm **SS2-TuA5 Low-Temperature Growth of Si/Si(111)-(7x7) by Femtosecond Pulsed Laser Deposition**, *I.A. El-Kholy, H. Elsayed-Ali*, Old Dominion University

Surface morphology during the growth of Si on Si(111)-(7x7) by femtosecond pulsed laser deposition (fsPLD) is studied using reflection high-energy electron diffraction (RHEED) at different temperatures. The growth of Si on Si(111) has received considerable attention as a model system of homoepitaxy. PLD is a deposition technique that uses much more energetic species (atoms and ions) compared to other physical vapor deposition (PVD), such as in molecular beam epitaxy. In PLD, the deposition process consists of periodic bursts of laser-generated plume followed by uninterrupted surface relaxation. This periodic nature of deposition differs from other PVD methods, and this could affect the growth mechanism. The use of ultrafast lasers vaporizes the target rather than melting it, thus minimizing the formation of particulates. In this work, in situ RHEED was used to study the dynamics of PLD of Si on Si(111)-(7x7). A Ti-sapphire laser (100-fs, 800-nm, 1 kHz) was used to ablate the Si target to generate a plume that deposit on a Si(111)-(7x7) kept at varying temperatures. The experiment was performed in an ultrahigh vacuum chamber at a residual gas pressure of 5×10^{-9} torr. It is observed that the decay of the RHEED pattern during deposition is due to the increase in the surface roughness. Epitaxial growth of Si/Si(111)-(7x7) at temperatures as low as 350°C was observed. For this substrate temperature, no change in RHEED patterns was observed after growth, with only reduction in intensity during deposition. This indicates that the growth mechanism was step-flow.

4:00pm **SS2-TuA8 Scanning Near Field Infrared Microscopy (SNIM) - Combining Topographical and Chemical Mapping of Bio Materials**, *M. Havenith*, Ruhr University Bochum, Germany **INVITED**

We have set-up a scanning near field microscope (SNIM) in Bochum. As radiation source serves an Infrared Opto Parametric Oscillator (IR-OPO) and a CO laser. This allows us to cover the chemically important frequency range of the amide bands and the C-H and O-H stretching region. In 2007 our group has reported chemical imaging of microstructure self-assembled monolayers (SAMs) with nanometre resolution¹ using SNIM. This study demonstrated the extreme sensitivity of SNIM which even allowed recording the IR spectrum of a single monolayer of a specific absorbing functional group (biotin). Our measurements were carried out on a microcontact printed line pattern of a monomolecular film of biotinylated alkythiolates. Whereas in conventional IR microscopy, about 1 μm thick layers of protein sample are required in order to record a full IR spectrum, here the IR fingerprint spectrum of approximately 30 000 biotin molecules in a 90 nm by 90 nm patch of 3.7 nm height were detected. Biotin can also be considered as a model system for more complex protein systems. Further

applications include the use for label-free analysis of biochips on the nano-scale. The possibility of simultaneously accessing topographic and spectroscopic information from biological nanostructures could be the basis for a new generation of nanodevices e.g. for medical diagnostics. As a proof-of-principle we demonstrate the feasibility of detecting hybridization reactions in nanostructured DNA-patches. For the DNA nanofabrication process we use nanografting which is a scanning probe microscopy based lithography technique. The nanografted single stranded nano structures can be clearly detected within the double stranded self assembled monolayers due to their distinct IR frequency response. Moreover, even nanografted double stranded nanostructures can be imaged since they have a higher packing density, yielding increased IR absorption in the corresponding amide band. This work is carried out in cooperation with the group of L. Casalis and G. Scoles at ELETTRA.

¹ I. Kopf, J.-S. Samson, G. Wollny, Ch. Grunwald, E. Bründermann, and M. Havenith, Chemical imaging of microstructured self-assembled monolayers (SAMs) with subwavelength resolution, *J. Phys. Chem. C*, 111 (23), 8166-8171 (2007).

4:40pm **SS2-TuA10 Non Statistical Patterns of Chemical Reactivity on Metals**, *A.L. Utz, D.R. Killelea*, Tufts University

Facile electron- and phonon-mediated energy exchange channels on metal surfaces have the potential to support rapid and extensive energy exchange during a reactive collision, but recent state-resolved reactivity measurements of methane's dissociative chemisorption on Ni have produced clear evidence for incomplete (non-statistical) energy redistribution prior to reaction. Examples include vibrational-mode selective chemistry (in which reactivity is influenced not only by the amount of vibrational energy available, but also by the identity of the excited vibrational state), the observation that vibrational and translational energy differ in their ability to activate reaction, and even bond-selective chemistry (selective excitation of the C-H stretch in CHD₃ prior to surface impact increased the C-H : C-D bond cleavage ratio among products nearly 100-fold relative to an isoenergetic ensemble of CHD₃ whose vibrations were statistically populated). We will describe a mechanistic framework for understanding the origin of observed non-statistical reactivity and predicting the propensity for such behavior in other systems. The model builds on numerous experimental and theoretical studies of intramolecular vibrational energy flow and quenching in the gas phase, in liquids, and at surfaces, and it focuses on the timescales for key energy exchange processes relative to reaction. It provides a qualitative explanation for observed reactivity patterns, intuitive guidance for understanding and predicting reactivity patterns, and it identifies attractive targets for future experimental and theoretical work to better understand and exploit these effects.

5:00pm **SS2-TuA11 Adsorption versus Interaction Strength: Analysis of Molecule-Surface Interactions of Organic Molecules on Pt and Pt-Sn Surfaces with HREELS and DFT**, *J. Haubrich*, University of Bonn, Germany, *D. Loffreda, F. Delbecq, Y. Jugnet, P. Sautet*, Ecole Normale Supérieure de Lyon, France, *C. Becker, K. Wandelt*, University of Bonn, Germany

Studies on catalysis such as the selective hydrogenation of α,β -unsaturated aldehydes on transition metal surfaces represent a challenge to both experimentalists and theoreticians. In order to elucidate the underlying elementary reactions, the assignment of the adsorption structures of complex molecules on model-catalyst surfaces is a fundamental step. Insight into the molecule-surface bonding of these structures is crucial for instance to understand the different hydrogenation activities and selectivities of multifunctional molecules on various catalysts. Furthermore introducing alloying effects to catalyst surfaces can change the properties of catalysts significantly and, thereby give rise to additional modifications of the molecule-surface interaction. Here we present a complementary experimental and theoretical study on the molecule-surface interaction of different organic molecules including ethene, butadiene and the α,β -unsaturated aldehydes crotonaldehyde and prenal on Pt(111) and two ordered Pt-Sn surface alloys. With the combination of HREELS (high-resolution electron energy loss spectroscopy) experiments carried out on the three model-catalysts and complimentary density-functional theory (DFT) calculations of vibrational spectra, we identified the stable adsorption structures on Pt(111) as well as the Pt₂Sn/Pt(111) and the Pt₃Sn/Pt(111) surface alloys. Surprisingly, we find that the changes in the vibrational shifts for corresponding structures on the three surfaces induced by the alloying cannot be satisfactorily correlated with the changes in the adsorption energies. However, with a detailed energetic analysis of the molecule-surface bonding, new insights on the interaction strength with the substrate are obtained that allow to rationalize the behavior of the vibrational properties.

5:20pm **SS2-TuA12 Examination of Force Interactions on Surfaces with Atomic Resolution Using Noncontact Atomic Force Microscopy**, *T.C. Schwendemann, B.J. Albers, M.Z. Baykara, N. Pilet, E.I. Altman, U.D. Schwarz*, Yale University

Interaction forces on the atomic scale govern the underlying physics of many fields of nanotechnology research, such as, catalysis, thin film growth, device fabrication, and tribology. Therefore, we present a method of atomic force microscopy which allows for the generation of 3D force maps of sample surfaces with atomic scale resolution. A homebuilt tuning fork based noncontact atomic force microscope (NC-AFM) facilitates the measurement of tip position and frequency shift that can be translated into force. Until recently, acquisition of surface forces on the atomic scale has been restricted to low resolution maps of single point force curves or 2D atomic resolution (xz) maps. The main difficulty in producing 3D force maps has been minimizing the drift of the instrument over the long acquisition times associated with 3D data collection. To address this issue, our low temperature ultrahigh vacuum NC-AFM was built with a high degree of thermal and mechanical stability. This stability has been demonstrated by our first 3D measurements on highly oriented pyrolytic graphite (HOPG). We chose HOPG as a test material in order to investigate the atomic scale origins of its qualities as a solid lubricant. Data was collected spanning several unit cells laterally and vertically from the attractive region to where no force interactions could be measured. A fine data mesh shows pN forces with less than 7 pm lateral and 1-2 pm vertical resolution. From this 3D data set, cuts along any plane can be plotted in 2D. Cuts in a plane parallel to the sample surface show atomic resolution. Cuts along the surface normal visualize how the atomic attractive force fields extend into vacuum. Now that this technique has been demonstrated it may serve for the further study of chemical force interactions. It is our intention to apply this technique to simple metal oxide surfaces to determine the chemical force interactions between the scanning probe tip and specific surface sites.

Authors Index

Bold page numbers indicate the presenter

— A —

Albers, B.J.: SS2-TuA12, 2
Altman, E.I.: SS2-TuA12, 2
Auerbach, D.J.: SS2-TuA1, 1

— B —

Baykara, M.Z.: SS2-TuA12, 2
Becker, C.: SS2-TuA11, 2

— C —

Campbell, V.L.: SS2-TuA4, **1**
Chen, N.: SS2-TuA4, 1
Cooper, R.: SS2-TuA1, 1

— D —

Delbecq, F.: SS2-TuA11, 2

— E —

El-Kholy, I.A.: SS2-TuA5, **1**

Elsayed-Ali, H.: SS2-TuA5, 1

— H —

Haubrich, J.: SS2-TuA11, **2**
Havenith, M.: SS2-TuA8, **1**
Huba, K.: SS2-TuA3, 1

— J —

Jugnet, Y.: SS2-TuA11, 2

— K —

Killelea, D.R.: SS2-TuA10, 2; SS2-TuA4, 1
Krix, D.: SS2-TuA3, **1**

— L —

Loffreda, D.: SS2-TuA11, 2

— N —

Nienhaus, H.: SS2-TuA3, 1

— P —

Pilet, N.: SS2-TuA12, 2

— R —

Rahinov, I.: SS2-TuA1, 1

— S —

Sautet, P.: SS2-TuA11, 2
Schwarz, U.D.: SS2-TuA12, 2
Schwendemann, T.C.: SS2-TuA12, **2**

— U —

Utz, A.L.: SS2-TuA10, **2**; SS2-TuA4, 1

— W —

Wandelt, K.: SS2-TuA11, 2
Wodtke, A.M.: SS2-TuA1, **1**