

Surface Science

Room 2004 - Session SS2-MoM

Gas-Surface Reaction Dynamics

Moderator: P.D. Johnson, Brookhaven National Laboratory

8:00am **SS2-MoM1 Biphasic Substrate-Adsorbate Energy Transfer Following Subpicosecond Photoexcitation**, *P. Szymanski, A.L. Harris, M.G. White*, Brookhaven National Laboratory; *N. Camillone III*, Brookhaven National Laboratory, Suffolk

Photodesorption of carbon monoxide molecules from a Pd(111) surface caused by femtosecond laser pulses was studied by two-pulse correlation measurements. The measured decay of the desorption yield with pump-probe delay reveals that the dynamics of energy transfer are independent of surface coverage and are biphasic, comprising two components with subpicosecond and 30-ps characteristic decay times. The relative contribution of the slower component to the total desorption yield is found to decrease as the difference between the desorption temperature and the surface temperature increases. This behavior is consistent with simultaneous excitation coupling from both electrons and phonons of the metal into the adsorbate-substrate bond. The strong contributions from two separate coupling mechanisms is distinct from that observed for CO desorption from other metals (e.g., Cu and Ru), where either fast or slow coupling predominates.

8:20am **SS2-MoM2 Influence of Film Thickness on the Reactions of Gas Phase Radicals with Self Assembled Monolayers**, *H. Fairbrother, J. Gorham*, Johns Hopkins University

The influence of chain length in the reactions of thin film assemblies with reactive gas phase species has been identified in studies designed to probe the modification of alkanethiolates by atomic hydrogen (AH). In these studies the change in chemical composition of four alkanethiolate self assembled monolayers (SAMs), octadecanethiolate, hexadecanethiolate, dodecanethiolate and nonanethiolate, as a result of exposure to atomic hydrogen have been studied in situ, using X-ray Photoelectron Spectroscopy. Reactions of atomic hydrogen with the native thiolate S atoms at the film/substrate interface are responsible for sulfur desorption and the formation of new C-S-C species. For each alkanethiolate, exposure to atomic hydrogen results in a loss of sulfur and carbon. The rate of sulfur loss from each SAM are well described by first order kinetics with a rate constant that increases with increasing chain length. This is consistent with the idea that sulfur desorption is controlled by the rate of atomic hydrogen permeation through the hydrocarbon overlayer. In the two shorter chain SAMs, the initial loss of carbon and sulfur is strongly correlated, indicative of a dominant role for the desorption of intact adsorbate chains and large alkyl sulfur fragments. In contrast, for octadecanethiolate and hexadecanethiolate SAMs the rate of carbon loss is dramatically reduced and the carbon and sulfur desorption kinetics are uncorrelated. In these longer chain SAMs the variation in the film's chemical composition as a function of AH exposure is consistent with the formation of a disordered carbonaceous overlayer, due to cross-linking reactions between adjacent hydrocarbon chains, before atomic hydrogen permeates to the film/substrate interface. Results from this investigation highlight the important role that film thickness can play in moderating the reaction kinetics in organized thin film assemblies.

8:40am **SS2-MoM3 Activated Dissociative Chemisorption: Distinguishing Between Statistical and Dynamical Behavior**, *I. Harrison*, University of Virginia **INVITED**

Progress towards achieving a unified kinetic picture of surface reactions has been uneven when nonequilibrium surface science and thermal equilibrium catalysis experiments have been compared and contrasted with electronic structure theory (EST) calculations of transition state characteristics. A simple, two to three parameter, microcanonical unimolecular rate theory (MURT) model of gas-surface reactivity has been able to largely close this "nonequilibrium gap" for several activated dissociative chemisorption reactions [e.g., H@sub2@ on Cu(111); CH@sub4@ on Ni(100), Pt(111), Ir(111), and Ru(0001); SiH@sub4@ on Si(100); and C@sub2@H@sub6@ on Pt(111)]. The MURT's ability to quantitatively predict and directly compare the results of disparate equilibrium and nonequilibrium experiments to one another and to the calculations of EST will be shown to open up some useful new opportunities to rigorously test and refine our understanding of reactive transition states and kinetics at surfaces. Identification of the essential role

of surface phonons and the approximate spectator status of rotational motion in the H@sub2@ dissociation dynamics on Cu(111) will be highlighted in this talk.

9:40am **SS2-MoM6 Vibrational Energy Flow in a Gas-Surface Reaction**, *D.R. Killelea¹, A.L. Utz*, Tufts University

Energy flow plays a central role in the activation of surface reactions. We measure how energy selectively deposited into the translational, rotational, and vibrational coordinates of methane influences S@sub 0@ on Ni(100) and Ni(111) to answer key questions about energy flow in this prototypical gas-surface reaction. Infrared laser excitation of CH@sub 4@ in a supersonic molecular beam prepares a microcanonical ensemble of reagents with well-defined internal and translational energies. We quantify reactivity for the state-selected reagents and observe non-statistical patterns of activation, including vibrational mode specificity. For example, the @nu@@sub 3@ C-H stretch is more reactive than the second overtone of the umbrella-bending mode, 3@nu@@sub 4@, even though 3@nu@@sub 4@ contains 30% more energy. On Ni(111) energy deposited in @nu@@sub 3@ activates dissociative chemisorption more than an equivalent amount of translational energy. To understand these results, we propose a framework for describing energy flow among the energetic degrees of freedom available to the molecule-surface reaction complex. Our model draws on and is consistent with descriptions of intramolecular vibrational energy flow in both the gas-phase and in liquids, but accounts for features unique to gas-surface reactivity. We focus on the characteristic timescales for energy flow and the molecule-surface interaction time. We conclude that for direct dissociative chemisorption of CH@sub 4@, there is insufficient time for full energy randomization among the energetic degrees of freedom in the molecule-surface reaction complex. Our model not only predicts vibrational mode-specific behavior - it also suggests a consistent explanation of surface temperature effects, explains the success of statistical theories to model ensemble-averaged reactivity even when energy flow is not statistical, and provides a framework for assessing the extent of energy flow in other gas-surface reactions.

10:20am **SS2-MoM8 Ultrafast Structural Dynamics in Complex Materials using Femtosecond Visible and X-ray Pulses**, *R.W. Schoenlein*, Lawrence Berkeley National Laboratory **INVITED**

Understanding the correlated interplay between atomic structure and electronic structure and properties is a fundamental challenge in condensed matter physics, particularly for correlated materials exhibiting strong coupling between charge, spin, orbit, and lattice vibrational degrees of freedom. Time-resolved measurements provide a new window to this problem by enabling the study of coupled interactions on time scales shorter than the underlying correlations. This talk will focus on recent ultrafast measurements of photo-induced phase transitions in transition-metal oxides, molecular complexes, and manganites in which the underlying mechanism of the phase transition is revealed by the time-scale of the dynamics. The talk will also discuss recent progress in the development and application of ultrafast x-ray techniques to the study of atomic and electronic structural dynamics in complex materials. X-rays are ideal probes of atomic structure, and offer important advantages for probing electronic structure as well (valence states, bonding geometry etc.) The application of x-ray structural probes on the time scale of a vibrational period, ~100 fs, is an important new tool for understanding complex materials.

11:00am **SS2-MoM10 Direct Probing of the Surface Dangling Bond by Means of Evanescent Wave Cavity Ring Down Spectroscopy**, *M.C.M. Van De Sanden, I.M.P. Aarts*, Eindhoven University of Technology, The Netherlands; *A.C.R. Pipino*, NIST; *W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands, Netherlands

The surface interaction of gas phase species plays an important role in crystal and thin film growth, chemical passivation and heterogeneous catalysis. Adsorbants, with usually a significant coverage, can be measured using scanning probe, optical or nuclear techniques, preferably in situ and real time. The surface kinetics however, are usually controlled through the creation of a so-called dangling bond. In this contribution we demonstrate a novel technique to probe surface dangling bonds directly and in real time. The method employed is based on evanescent wave cavity ring down absorption spectroscopy using an ultralow-loss fused silica monolithic folded resonator.¹ On the curved surface of the folded resonator a thin hydrogenated amorphous silicon (~800 nm) is grown by means of hot wire assisted chemical vapor deposition. The broad band

¹ Morton S. Traum Award Finalist

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absorption feature of the dangling bond is probed between 1170 and 1245 nm with an unprecedented sensitivity. Absorption losses as low as 10^{-7} per laser pulse can be measured, corresponding with a surface dangling bond coverage of 10^{-6} . The a-Si:H film was dosed using a calibrated atomic hydrogen. Uptake curves were measured as function of atomic hydrogen flux. The saturated surface coverage measured was around 5×10^{-4} for an H-flux of 2×10^{14} cm $^{-2}$ at a measured abstraction probability from the initial up-take curves of around 0.01 ± 0.003 . These results, which confirm previous reports on H saturated surfaces, might point towards a hot-precursor related adsorption-desorption mechanism. However we clearly observe a saturated surface coverage that is H-flux dependent, in contrast with predictions based on Langmuir-Hinshelwood or Eley-Rideal mechanism. In addition we report on the self passivating effect of a-Si:H surfaces after the dosing with atomic hydrogen has ended.

@FootnoteText@ @footnote 1@ Aarts et al. PRL 95 166104 (2005).

11:20am **SS2-MoM11 Image and Image-Derived States Formed by Molecular Thin Film Structures**, *E.T. Jensen*, University of Northern B.C., Canada; *L. Sanche*, Universite de Sherbrooke, Canada

Electron transport through and interaction with molecular thin films is an area of much current interest. In this work, electron image states formed at molecular interfaces have been used to enhance the trapping of low energy electrons by adsorbed 'detector' molecules. @footnote 1@ A magnetically collimated low energy electron beam (electron energies between 0 and 10eV) is incident upon prepared molecular thin films, and the formation of stable anions at the surface are monitored using a charge trapping technique. @footnote 2@ We have studied thin films prepared on a cold ($T=15K$) polycrystalline platinum substrate. Molecular films are grown on top of a 10ML thick Kr spacer layer, to isolate the film from the metal substrate. On this Kr/Pt substrate we have grown various thin molecular films (1-10ML thick) that support image states. We have studied image states formed at the surface of methanol, 1-butanol, n-octane and difluoromethane thin films. Low energy electron transmission spectra show that all these films display a conduction band gap near the vacuum level, which is crucial in supporting long-lived image states. To detect the image states formed by these molecular thin films, we introduce submonolayer quantities of 'detector' molecules that can be dissociated by low energy electrons to create stable anions (CH_3I , CH_3Br , CH_3Cl) or which support stable molecular anions (CO_2). We have studied image state enhanced electron trapping at the molecular film-vacuum interface. We have also created and studied molecular film 'quantum well' type structures in which the detector molecules are placed in a Kr spacer between two molecular thin films- in the region between two films an image-state derived quantum well state can be identified. @FootnoteText@ @footnote 1@ K. Nagesha and L. Sanche, Phys. Rev. Lett. 81, (1998) 5892. @footnote 2@ K. Nagesha, J. Gamache, A.D. Bass and L. Sanche, Rev. Sci. Inst. 68, (1997) 3883.

11:40am **SS2-MoM12 Reaction Dynamics of NO Gas on Iron Phthalocyanine Thin Films**, *N.L. Tran*, University of California at San Diego, Unites States; *S.R. Bishop*, *G.C. Poon*, *A.C. Kummel*, University of California at San Diego

Metallophthalocyanines (MPcs) have been proposed for use in organic-based chemical field effect transistor (chem-FET) detectors for the measurement of ambient gases such as NO_x , NH_3 and O_3 . However, the mechanisms of the reaction between these gases and MPc thin films have not been studied. We have investigated the reaction dynamics between NO gas and a monolayer iron phthalocyanine (FePc) on a Au(111) substrate. Sticking probabilities of a molecular beam of NO were measured on both clean Au(111) and ordered monolayer FePc deposited on clean Au(111). The sticking probabilities were measured both as a function of beam energy (0.09eV - 0.4eV) and surface temperature (125K - 325K). The sticking probability of NO onto the FePc film saturates at 3% of a ML for all surface temperatures and all incident kinetic energies consistent with the final chemisorption site being confined to the FePc metal center. In contrast to the saturation coverage, the sticking probability is large (40%) at low surface temperature and low incident kinetic energy and decreases linearly with increasing surface temperature but is independent of beam energy above 0.26eV. Temperature dependent sticking which is independent of kinetic energy is not consistent with simple models of direct chemisorption nor precursor mediated chemisorption. Instead, the data is consistent with NO sticking onto the monolayer FePc via multiple precursor-mediated physisorption pathways in which the NO traps onto the aromatic rings and then diffuses to the metal center on FePc. Density functional theory simulations of NO binding onto

the FePc molecule also support this theory. These calculations show a multi-step absorption mechanism in which NO initially binds to the inner ring nitrogens and subsequently migrates to the deep chemisorption well on the metal centers for FePc.

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