Thursday Afternoon, October 31, 2013

Surface Science
Room: 202 A - Session SS2-ThA

Surface Dynamics and Non-adiabatic Processes
Moderator: R.A. Bartynski, Rutgers University

2:00pm SS2-ThA1 Angle-Resolved Dissociative Sticking Coefficients of Light Alkanes on Pt(111) Measured with Effusive Molecular Beams, *J.K. Navin, S.B. Donald, I.A. Harrison*, University of Virginia
Angle-resolved dissociative sticking coefficients (DSCs) were measured for a series of small alkanes on Pt(111) using effusive molecular beams. Measurements relevant to both thermal equilibrium ($T_g = T_s$) and non-equilibrium ($T_g \neq T_s$) conditions were obtained. A precursor mediated microcanonical trapping (PMMT) model was useful in analyzing and comparing different kinds of experiments. The thermal DSC for methane dissociative chemisorption on Pt(111) at 700 K varied sharply around the direction of the surface normal as $S(700 \text{ K}, \varphi) = 8.2 \text{ x } 10^{-5} \cos^{14.5}(\varphi)$. Successful modeling of this methane DSC behavior, consistent with existent supersonic molecular beam experiments involving rotationally cold molecules, required that translation parallel to the surface and rotations be treated as a spectator degree of freedoms and that the vibrational efficacy relative to normal translational energy be $\eta_v = 0.4$. Across the series of alkanes, methane, ethane, and propane, the angular distributions of the thermal DSCs broadened significantly. The only angle-dependent energy that promotes thermal dissociative chemisorption of alkanes is molecular normal translational energy, $E_n = E_t \cos^2(\varphi)$, which should become less important as the vibrational energy of the impinging molecules increases with increasing molecular size. The bounds that the thermal angle-resolved DSCs place on theoretical models of alkane reactivity will be discussed.

2:20pm SS2-ThA2 Thermal Non-Equilibrium Desorption of $^{13}CO_2$ Formed by the Decomposition of Formate on Cu Surfaces, *J. Quan, T. Kondo, M. Sakurai, J. Nakamura*, The University of Tsukuba, Japan
It is well known that formate (HCOO*) specie is the important intermediate for methanol synthesis by hydrogenation of CO_2 on copper catalysts. Because the formate synthesis by reaction of CO_2 with adsorbed hydrogen atom has been suggested to be an Eley – Rideal type mechanism [1], we try to clarify the dynamics of formate decomposition on Cu（110）, Cu（100）and Cu（111）surfaces in this study. That is, both formate synthesis and formate decomposition are expected to be thermal non-equilibrium processes. We have thus measured angle-resolved temperature programmed desorption (AR-TPD) of CO_2 formed by decomposition of formate. Formate was prepared by decomposition of ^{13}C-formic acid ($H^{13}COOH$) on oxygen pre-adsorbed or oxygen-free Cu(110), Cu(100) and Cu(111) surfaces. AR-TPD experiments were then carried out for $^{13}CO_2$. The signal intensity of $^{13}C^{16}O_2$ in distribution was plotted for each polar angle in the range -80° to 80°(5° as interval angle) from TPD spectrum. It is found that identical sharp distributions of $^{13}CO_2$ were observed Cu(110), Cu(100) and Cu(111) surfaces, showing distribution normal to the surfaces with the function of $\cos^8\theta$. These results indicate that the decomposition of formate is a thermal non-equilibrium process, in which CO_2 molecules desorb with hyper-thermal energy due to a repulsive force from the surfaces. It is also suggested that the local structures just before the CO_2 desorption near the transition states (TS) are the same on Cu（110）, Cu（100）and Cu（111）. That is, ^{13}C of ^{13}COO is bound with a hydrogen adatom, while the O-Cu bond has been already broken just before the CO_2 desorption. The TS structures may be free to rotate and therefore desorbed $^{13}CO_2$ distribution is insensitive to the surface structure. The structure insensitivity is consistent with that measured for the kinetics of formate synthesis. Density functional theory (DFT) calculations are also consistent with the proposed model. [1] H. Nakano, J. Nakamura et al., J. Phys. Chem. B, 105 (2001) 1355-1365.

2:40pm SS2-ThA3 RRKM Simulation of Hydrogen Dissociation on Cu(111): Addressing Dynamical Biases, Surface Temperature, and Tunneling, *S.B. Donald, I.A. Harrison*, University of Virginia
The effects of dynamics, surface temperature, and tunneling on the dissociative chemisorption of hydrogen on Cu(111) are explored using a dynamically-biased precursor mediated microcanonical trapping (d-PMMT) model. Transition state vibrational frequencies were taken from recent GGA-DFT electronic structure calculations and the model's few remaining parameters were fixed by optimizing simulations to a limited number of quantum-state-resolved associative desorption experiments. The d-PMMT model reproduces a diverse variety of dissociative chemisorption and associative desorption experimental results, and, importantly, largely captures the surface temperature dependence of quantum-state-resolved

dissociative sticking coefficients. Molecular translational energy parallel to the surface was treated as a spectator degree of freedom. The efficacy of molecular rotational energy to promote dissociation, relative to normal translational energy, varied monotonically from -45% to 33% as the rotational energy increased. The molecular vibrational and surface phonon efficacies were 60%. Efficacies did not vary with isotope change from H_2 to D_2. The thermal dissociative sticking coefficient for $H_2/Cu(111)$ is predicted to vary as $S(T) = S_0 \exp(-E_a/RT)$ where $S_0 = 0.075$ and $E_a = 49.2$ kJ/mol over the 300 K $\leq$ T $\leq$ 1000 K temperature range. Dynamical effects are significant and suppress S(T) by ~2 orders of magnitude as compared to statistical expectations. For thermal dissociative chemisorption of $H_2/Cu(111)$ at 1000 K, a temperature of catalytic interest, normal translational energy is calculated to provide 74% of the energy necessary to react, surface phonons 17%, molecular rotation 5%, and vibration 4%. Tunneling is calculated to account for 13% of S(T) at 1000 K, but more than 50% at temperatures below 400 K.

3:00pm SS2-ThA4 Ultrafast Probing of Chemical Reactions using X-rays from a Free-Electron Laser, *J.L. LaRue*, SLAC National Accelerator Lab, *M. Dell'Angela,* Univ. of Hamburg, Germany, *M. Beye,* HZB für Mat. und Energie/Elektronenspeicherring BESSY II, Germany, *R. Coffee,* SLAC National Accelerator Lab, *A. Föhlisch,* HZB für Mat. und Energie/Elektronenspeicherring BESSY II, Germany, *J. Gladh,* Stockholm Univ., Sweden, *T. Katayama, S. Kaya, J.A. Sellberg,* SLAC National Accelerator Lab, *A. Møgelhøj,* Technical Univ. of Denmark, *D. Nordlund, J.K. Nørskov,* SLAC National Accelerator Lab, *H. Öberg,* Stockholm Univ., Sweden, *H. Ogasawara,* SLAC National Accelerator Laboratory, *H. Öström, L.G.M. Pettersson,* Stockholm Univ., Sweden, *W.F. Schlotter,* SLAC National Accelerator Lab., *W. Wurth,* Univ. of Hamburg, Germany, *M. Wolf,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *A. Nilsson*, SLAC National Accelerator Lab.
The femtosecond dynamics of CO adsorbed on a Ru(0001) surface after excitation by an optical laser have been studied using the Linac Coherent Light Source (LCLS) free electron x-ray laser. Changes in the occupied and unoccupied electronic structure were monitored using ultrafast soft x-ray absorption and emission spectroscopy. We found that the CO molecules, upon excitation by the optical laser, are excited to a weakly adsorbed precursor state occurring on a time scale of >2 ps, and at longer timescales, desorbed from this precursor state. Ab initio molecular dynamics simulations of CO adsorbed on Ru(0001) were performed at 1500 and 3000 K providing insight into the desorption process. Within the first couple picoseconds, the metal-adsorbate coordination is initially increased due to hot-electron-driven vibrational excitations. This process is faster than, but occurs in parallel with, the transition into the precursor state. With resonant x-ray emission spectroscopy, each of these states can be selectively probed and the optical laser fluence dependent transient populations can be determined. At high optical laser fluences, a large fraction of the molecules (30%) were trapped in the transient precursor state that precedes desorption. We observed electronic structure changes that are consistent with a weakening of the CO interaction with the substrate. About half the molecules in the precursor state desorbed from the surface while the other half return to the chemisorbed state. We calculated the free energy of the molecule as a function of the desorption reaction coordinate using density functional theory, including van der Waals interactions. Two distinct adsorption wells - chemisorbed and precursor state separated by an entropy barrier - explain the anomalously high prefactors often observed in desorption of molecules from metals.

3:40pm SS2-ThA6 Dynamics of Electron Transfer and Exciton Formation at Interfaces, *M. Wolf*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**
We have studied the ultrafast dynamics of photoinduced electron transfer and solvation processes at the water ice-metal interface and focus here on the effect of co-adsorbed alkali ions (Na, K, Cs). Femtosecond time-resolved two-photon-photoemission (2PPE) spectroscopy provides direct access to elementary processes like electron injection and the subsequent solvation dynamics which competes with the electron transfer back to the Cu(111) substrate. In particular, we study the electronic structure changes and ultrafast dynamics for the bulid-up of a solvation shell (up to 6 water molecules) around individual alkali atoms at the metal surface and compare with electronic structure calculations. For ice mulitlayers doped with alkali ions we observe the formation of longlived electron alkali-water complexes.

As an example for a hybrid system of inorganic and organic semiconductors we investigate the electronic structure and dynamics at the ZnO(10-10) surface and the influence of hydrogen and pyridine adsorption. Hydrogen termination leads to the formation a metallic surface band, whereas pyridine adsorption results in a quite substantial work function reduction (up to 2.9

eV), which may be useful for controlling the energy level alignment at inorganic/organic interfaces. Furthermore we directly monitor the ultrafast relaxation of hot photocarriers in the ZnO conduction band and the subsequenst formation of an excitonic state at the ZNO surface on ps timescales.

4:20pm SS2-ThA8 Single Molecule Spectroscopy and Reactions at Surfaces, *M. Kawai*, The University of Tokyo, Japan, *Y. Kim*, RIKEN, Japan, *N. Takagi*, The University of Tokyo, Japan **INVITED**
Ultimate spatial resolution of scanning tunneling microscope (STM) enables us to observe the inner electronic, vibrational [1-6] and spin [7-9] structures of a molecule adsorbed on solid surfaces. Vibrational spectrum of a single molecule provides useful information not only for the chemical identification of the molecule [1] but also for investigating how molecular vibrations can couple with the relevant dynamical processes [2-6], where the response of vibrationally mediated molecular motion to applied bias voltage, namely an "action spectrum", can reveal vibrational modes that are excited through STM inelastic tunneling processes, because the molecular motion is induced only *via* the inelastic tunneling processes [3-5]. Molecular spin can couple with electrons of metal substrates. Depending on the strength of the coupling spin state of the molecule changes. Examples are given for Iron phthalocyanine (Fe-Pc) adsorbed on Cu, Au and Ag. With strong coupling with Cu(110) the spin is completely killed whereas if decoupled as on Cu(110) 2x1-O, spin survives with change in the direction of easy axis [7]. On Au weak coupling leads to appearance of Kondo state, where a competition between the RKKY interaction affects the spin state [8]. Kondo state of FePc on Au depends on the adsorption site, where the difference was originating from the coupling with the substrate electrons [9-10].

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5:00pm SS2-ThA10 The Role of Vibrationally Hot Precursors in Methane Activation on Ir(111) and Ir(110), *A.L. Utz, E. Peterson, E. Dombrowski, E. High*, Tufts University
Vibrationally excited molecules can play an important role in methane activation on transition metal catalysts. This talk will focus on the reactivity of vibrationally excited methane molecules physisorbed to the surface. Under thermal reaction conditions typical in a steam reforming reactor, over half of the methane molecules are vibrationally excited, but their average translational energy is low enough that their trapping probability is significant. We use seeding techniques and molecular beam scattering methods to control the translational energy of the methane molecules incident on the surface, and infrared laser excitation of molecules in the molecular beam to control the amount and type of vibrational excitation. We find that vibrationally hot molecules can undergo reaction on low-index Ir surfaces via a precursor-mediated mechanism even in the presence of efficient vibrational quenching channels on the metal surface. In another set of experiments we explore how methane molecules in the ground vibrational state are activated while physisorbed to a hot surface.

In contrast to prior suggestions, this work suggests that an increase in reactivity with gas temperature may not be an automatic signature for a direct reaction mechanism where methane dissociates in a single collision. High gas temperatures also result in significant populations of vibrationally excited molecules whose additional internal energy may enhance their precursor-mediated reactivity. Our ability to control independently the translational and vibrational energy of the methane reagent and the surface temperature allows us to deconvolute these contributions to reactivity and

more clearly reveal the mechanistic basis for methane activation under conditions typical in thermal processing.

5:20pm SS2-ThA11 Vibrational Efficacy in Methane Dissociative Chemisorption Dynamics, *S.B. Donald, I.A. Harrison*, University of Virginia
Dynamics play an important role in the activated dissociative chemisorption of methane and can modulate the thermal reactivity by about an order of magnitude as compared to statistical expectations based on energetics alone. A dynamically-biased precursor mediated microcanonical trapping (d-PMMT) model of activated dissociative chemisorption has sufficed to quantitatively replicate the behavior of methane interacting with a number of metal surfaces (M) for a variety of non-equilibrium and thermal equilibrium experiments. It was found that molecular translation parallel to the surface and rotations are spectator degrees of freedom and vibrational energy is typically less efficacious than translational energy directed along the surface normal in promoting reactivity [e.g., the vibrational efficacy relative to normal translational energy is $\eta_v = 0.4$ for CH_4/Pt(111)]. This latter kind of dynamical effect is well-documented for gas-phase atom + diatomic molecule reactions where it is codified by the "Polanyi rules" which state that "early" transition state barriers are preferentially surmounted by translational energy and "late" barriers by vibrational energy. The threshold energy for chemisorption, E_0, and the thermally state averaged vibrational efficacy, η_v, derived from d-PMMT analysis of different CH_4/M experiments are shown to have interesting and systematic correlations with the results of GGA-DFT electronic structure calculations of CH_4/M transition state properties as M is varied. The Polanyi rules apparently extend well to the CH_4/M chemistry and may thereby serve to guide ab initio predictions of experimental dissociative sticking coefficients.

5:40pm SS2-ThA12 NO Formation in Eley-Rideal Reactions with Hyperthermal N Atoms, *T. Zaharia*, Materials innovation institute (M2i), Netherlands, *A.W. Kleyn*, University of Amsterdam, Netherlands, *M.A. Gleeson*, FOM Institute DIFFER, Netherlands
Almost all chemical reactions at surfaces proceed via the Langmuir-Hinschelwood mechanism. In such a reaction all reactants equilibrate to the surface before meeting by diffusion and reacting. By contrast, Eley-Rideal reactions are prompt reactions occurring on impact of an atom or molecule from the gas phase. In environments where hyperthermal reactive atoms are present such as on spacecraft, such Eley-Rideal type reactions can be expected. However, these have not yet been observed under well-defined conditions for heavy atoms such as nitrogen. Only for hydrogenic reactions Eley-Rideal reactions have been demonstrated under UHV conditions. In this work we present results of a systematic study into the importance of such reactions and report the first observations thereof.

In the experiments an effusive beam of hyperthermal nitrogen atoms is aimed at a Ru(0001)-O(2x1) surface at an angle of 60 degrees from the surface normal. Measurements of the angular distribution for Argon scattering under the same conditions have revealed that this surface is atomically flat and uncorrugated. Upon N-atom impact hyperthermal (4 eV) NO is detected. The angular distribution is peaked in the forward direction with a peak at 30 degrees from the normal, indicating that part of the N-atom parallel momentum is conserved in the NO forming collision. These are strong signatures of a prompt surface reaction.

To check the efficiency of the reaction, the time-of-flight spectra of the NO produced were measured for successive intervals. It became clear that fast NO was no longer produced, even though NO is still present in the back ground. From the decay of the NO production rate as a function of time the reactive cross section for the N+O=> NO reaction could be determined. It is about 2 Å^2. Such a high cross section is another evidence for an Eley-Rideal reaction.

Prompt reactions can be used to specifically remove adsorbates from surfaces. We will demonstrate that not only O-atoms but also N-atoms can be removed from surfaces.

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