

Wednesday Afternoon, October 21, 2015

Surface Science

Room: 112 - Session SS+AS-WeA

Surface Dynamics, Non-Adiabaticity, and Single Molecule Phenomena

Moderator: Eddy Tysoe, University of Wisconsin-Milwaukee

2:20pm **SS+AS-WeA1 Benchmarking Theory with Vibrational State Resolved Reactivity Measurements**, Arthur Utz, E. Peterson, E. Dombrowski, E. Nicotera, E. High, Tufts University

Electronic structure calculations provide predictions of energy thresholds for a wide range of surface chemical reactions, and they are the basis for significant advances in our understanding of surface reactivity. Despite the central role these calculations and their predictions play, testing the absolute accuracy of these calculations with direct experimental measurements has proven to be challenging.

The presentation will focus on using the results of state-resolved beam-surface scattering measurements to benchmark theoretical predictions. We find that when these measurements are performed on a cold surface, we observe sharp energetic thresholds for reaction. These observations result from our ability to control and vary precisely all energetic degrees of the system. These experimentally measured threshold energies can be compared directly with both electronic structure calculations, as well as with quantum dynamics predictions of chemical reactivity. We will compare experimental results for methane dissociation on Ni(111) with recent computational predictions from the Jackson group to illustrate this approach. We will also provide an update on our work extending this approach to other molecule-surface systems.

2:40pm **SS+AS-WeA2 Confirming the role of Hydrogen Bonding in Electron-promoted Desorption at Water Ice Surfaces**, D. Marchione, A.G.M. Abdulgalil, M.P. Collings, Martin McCoustra, Heriot-Watt University, UK

We have previously reported observations of large ($>10^{-16}$ cm²), low-energy (<500 eV), electron-promoted desorption cross-sections for benzene (C₆H₆) molecules adsorbed on the surface of amorphous solid water [1]. We will now report on the extension of this work to other molecular solids exhibiting varying degrees of hydrogen bonding within the molecular solid itself and between the solid surface and adsorbed benzene; specifically we have repeated our measurements employing substrates comprised of solid methanol (CH₃OH) and diethyl ether (CH₃CH₂OCH₂CH₃). Our report will detail our studies of the structure of adsorbed layers of C₆H₆ on the molecular solids and demonstrate the crucial role of hydrogen bonding in propagating electronic excitation to the solid-vacuum interface where C₆H₆ desorption can occur. Competitive electron-promoted chemistry in the form of H₂ formation will also be reported. Conclusions related to the impact of these observations on the early phase of icy interstellar grain chemistry will be discussed.

[1] Highly efficient electron-stimulated desorption of benzene from amorphous solid water ice, J. D. Thrower, M. P. Collings, F. J. M. Rutten, and M. R. S. McCoustra, *Chem. Phys. Lett.*, 2011, **505**, 106–111.

3:00pm **SS+AS-WeA3 Strategic Applications of the Vibrational Dynamics of the Outer Layer of Metal Nanoparticles**, Marisol Alcantara Ortigoza, University of Central Florida **INVITED**

The structure characterization, stability and thermal properties of nanoparticles (NPs) are topics of fundamental and technological significance. This information, however, is not always readily available from experiment. Moreover, the vibrational density of states VDOS of small (<2 nm) metal NPs definitely does not have a quadratic decay at the low-frequency end, for which the thermal properties cannot be obtained from the VDOS as Debye proposed in 1912. The features particular to the VDOS of NPs will be rationalized in terms of the charge density distribution around low-coordinated atoms, the quasi-radial geometric distribution of NPs, force constant variations, degree of symmetry of the nanoparticle, discreteness of the spectrum, and the confinement of the eigenmodes. I will present an explanation and application of the enhanced low- and high energy tails of the vibrational density of states (VDOS) of nanoparticles with respect to their bulk counterparts, as well as show that the eigenmodes defining the two extremes of the VDOS are not that alien to widely studied surface phonons. I will show that the high- and low-energy tails of the VDOS of NPs may be a powerful tool to reveal information about their chemical composition and geometric structure of small NPs. For

example, the size of the confinement gap at the low-frequency end of the VDOS and the extent by which the high-frequency end surpasses the bulk limit may indicate whether a NP is bulk-like or non-bulk-like and the extent to which it is disordered or segregated. Regarding thermal properties, I will also show that for NPs with a largely discrete VDOS, the frequency of their fundamental mode may largely determine their thermal properties.

4:20pm **SS+AS-WeA7 An Accurate Full-Dimensional Potential Energy Surface for H at Au(111): The Importance of Nonadiabatic Electronic Excitation in Energy Transfer and Adsorption**, S.M. Janke, A. Kandratsenka, Daniel Auerbach, A.M. Wodtke, Max Planck Institute for Biophysical Chemistry, Germany

We have constructed a potential energy surface (PES) for H atoms interacting with *fcc* gold based on the form of the PES in Effective Medium Theory. The PES was adjusted to match energies calculated by DFT in many configurations, including many with the Au atoms displaced from their lattice positions. It describes both the interatomic forces and electron densities in *full dimension* with the accuracy of the *ab initio* energies used in its construction. Calculations describing the motion of H and Au atoms using this full dimensional adiabatic PES agree with results obtained previously using *Ab Initio* Molecular Dynamics, demonstrating the accuracy of the PES for configurations occurring in the scattering of H atoms from a surface at finite temperature.

The analytic expression for the total energy contains the embedded electron density leading to a self-consistent approach to simulating nonadiabatic trajectories. We find that nonadiabatic electron-hole pair excitation is the most important energy loss pathway for the H atom. The calculated energy distributions for scattered H atoms are in reasonable agreement with experimental results that are just becoming available, and determines the probability and mechanism for its adsorption. Analysis of trajectories calculated with and without nonadiabatic energy dissipation shows the adsorption or sticking probability as well as the mechanism of H atom adsorption is changed dramatically by nonadiabatic energy transfer

4:40pm **SS+AS-WeA8 STM Characterization of Quasi-one Dimensional C₆₀ Nanostructures on Rippled Graphene**, C. Chen, H. Zheng, A. Mills, Chenggang Tao, Virginia Tech

Highly ordered one-dimensional (1D) molecular configurations are excellent model systems and prototypes of 1D quantum confinement of electronic states, and thus have potential importance in electronic nanodevices, spintronics and solid-state quantum computation. Due to the spherical geometry of C₆₀ molecules, it has been challenging to experimentally realize quasi-1D C₆₀ nanostructures, a highly anisotropic configuration. We will present our recent scanning tunneling microscopy (STM) characterization of novel quasi-1D C₆₀ nanostructures on rippled graphene. Through careful control of the subtle balance between the linear periodic potential of rippled graphene and the C₆₀ surface mobility, C₆₀ molecules can be arranged into a 1D C₆₀ chain structure with widths of two to three molecules. At a higher annealing temperature, the chain structure transitions to a more compact hexagonal close packed quasi-1D stripe structure. We will also discuss our scanning tunneling spectroscopy (STS) measurements on this hybrid system.

5:00pm **SS+AS-WeA9 Classical and Quantum Description of Ion Desorption from Ionic Crystals**, Leszek Markowski, University of Wrocław, Poland

It is well known that irradiation of the solid with electrons or photons can cause its decomposition. This process, or, more adequately processes, is very fast (typically finalized within a time shorter than 10⁻¹⁴ s) and is realized mainly by desorption of atoms or ions. Unfortunately, until now, existing models still do not give a proper value of the desorption yield and, simultaneously, a correct kinetic-energy distribution of emitted particles, as compared to the experimental observations.

In this talk a classical, quasi-quantum and quantum description of the positive ion desorption from ionic crystal surface, in which three potentials are involved, will be discussed and compared. It will be shown that the quantum description allows to explain some effects observed experimentally, such as a periodicity of small oscillations on the kinetic energy distribution (KED) curves (predicted by Wave-Packet Squeezing model) and emission through a temporarily existing potential barrier from the temporary bounded states located above the vacuum level. Moreover, analysis method of the ion KED oscillation and the fitting procedure which allows to determined a final effective desorption potential will be presented.

For two examples discussed, Li⁺ desorption from LiF and Na⁺ desorption from NaCl, desorption from two desorption sites can be distinguished – dominating ion desorption channel from adatom sites (more than 95%) and

marginal one from the sites in the first surface layer. For the second desorption channel neighboring negative ions, due to surface relaxation lying in the first surface layer slightly above positive one, can act as a two-dimensional array of rosette-like apertures. In consequence, positive ions after passing through them may form diffraction pattern.

Finally, it appears that when desorption process is described using three potentials both the ions desorption efficiency and their kinetic-energy distribution are in agreement with the experimental results.

5:20pm **SS+AS-WeA10 Spin and Isotope Effects on Molecular-Hydrogen Adsorption on Pd(210)**, *H. Kobayashi, S. Ohno, M. Wilde*, University of Tokyo, Japan, *M. Matsumoto*, Tokyo Gakugei University, Japan, *S. Ogura, Katsuyuki Fukutani*, University of Tokyo, Japan

Molecular hydrogen is physisorbed on flat metal surfaces via van der Waals interaction. By taking advantage of the fact that molecular hydrogen exists in nuclear-spin isomers of ortho and para species [1], we have shown the interaction potential on Ag(111) is anisotropic with a slight perpendicular preference [2]. The Pd(210) surface has a step-like structure consisting of alternately aligned (100) and (110) terraces, and it has been shown that H₂ is rather strongly adsorbed on H-covered Pd(210) with a significant contribution of orbital hybridization [3]. On the other hand, it has been suggested that molecularly adsorbed species could be important for hydrogen absorption into the interior of Pd surfaces [4]. In the present study, we have investigated the adsorption of H₂ and D₂ on the Pd(210) with temperature-programmed desorption (TPD) combined with resonance-enhanced multi-photon ionization (REMPI).

When Pd(210) was exposed to H₂ at 115 K, TPD revealed a desorption peak at 180 K (α -peak) originating from the adsorbed state as well as a peak at 280-320 K (β -peak) due to chemisorbed H. From the uptake rate of the α -peak, the absorption probability of H on Pd(210) was estimated to be 3×10^{-3} . When the surface was exposed to either H₂ or D₂ at 45 K, on the other hand, an additional TPD peak was observed at about 70 K (γ -peak), which was attributed to molecular adsorption. While a small difference between H₂ and D₂ was observed for the β -peak, the γ -peak temperature of D₂ was found to be higher than that of H₂ by 9 K, which corresponds to the difference in the adsorption energy of about 20 meV. Assuming that this difference is due to the zero-point energy difference in the adsorption potential, the adsorption potential was analyzed in terms of the Morse potential. By applying REMPI-TPD, furthermore, the TPD spectra of ortho-H₂ in the rotational state of $J=1$ and para-H₂ in $J=0$ were state-selectively measured. The desorption temperature of ortho-H₂ was found to be higher than that of para-H₂ by about 4 K, which corresponds to a difference in the adsorption energy of about 10 meV. We discuss that this large energy difference between the ortho and para species originates from the potential anisotropy on the basis of the first-order perturbation.

[1] K. Fukutani, T. Sugimoto, Prog. Surf. Sci. 88, 279 (2013).

[2] T. Sugimoto, K. Fukutani, Phys. Rev. Lett. 112, 146101 (2014).

[3] P. K. Schmidt et al., Phys. Rev. Lett. 24 87, 096103 (2001).

[4] S. Ohno et al., J. Chem. Phys. 140, 134705 (2014).

5:40pm **SS+AS-WeA11 Eley-Rideal Typed Mechanism of Formate Synthesis by Hydrogenation of Carbon Dioxide on Cu Surfaces**, *J. Quan*, University of Tsukuba, Japan, *T. Ogawa*, University of Tsukuba, Japan, *T. Kondo*, University of Tsukuba, Japan, *G. Wang*, Nankai University, China, *Junji Nakamura*, University of Tsukuba and ACT-C, Japan

Methanol synthesis by hydrogenation of CO₂ using Cu catalysts is one of the promising reactions to convert CO₂ into useful chemicals. Formate species is the pivotal intermediates formed as the initial step of CO₂ hydrogenation (CO₂ + H_a → HCOO_a). The reaction rate of formate synthesis is very low and the reaction probabilities are about 10⁻¹² at 340K. Our previous kinetic measurements have suggested that formate is synthesized via Eley-Rideal typed mechanism, in which CO₂ molecules directly attack adsorbed hydrogen atoms on Cu surfaces. The structure insensitivity observed for formate synthesis experiments on Cu(111), Cu(100), and Cu(110) were well explained by the Eley-Rideal mechanism based on DFT calculations. In addition, sharp angular desorptions of CO₂ have been observed for formate decomposition as the reverse reaction of formate synthesis, indicating thermal non-equilibrium reaction. In the present study, we performed molecular beam experiments to prove the Eley-Rideal typed mechanism, in which CO₂ molecules with controlling vibrational and translational energies were reacted with adsorbed hydrogen on cold Cu(111) and Cu(110) surfaces (T_s = 150-215 K). We confirmed the formation of formate species on Cu(111) and Cu(110) with reaction probabilities of 10⁻⁵ by heating nozzle above 1000 K, while no formate is formed at nozzle temperatures below 1000 K. The results indicate the Eley-Rideal typed mechanism with thermal non-equilibrium character. DFT calculations also reproduce the Eley-Rideal typed mechanism, in which

vibrational excitations of CO₂ are required to overcome the barrier of formate synthesis.

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