Surface Science
Room 104D - Session SS1+AS+HC+NS-TuM

Surface Dynamics, Non-Adiabaticity, and Theory and Modeling of Surface and Interfacial Phenomena

Moderator: Greg Kimmel, Pacific Northwest National Laboratory

8:00am **SS1+AS+HC+NS-TuM1 Graphene-Semiconductor Catalytic Nanodiodes for Quantitative Detection of Hot Electrons Induced by a Chemical Reaction***, **Hyosun Lee**[*],* KAIST & IBS, Republic of Korea*; I. Nedrygailov,* IBS & KAIST, Republic of Korea*; Y.K. Lee, C. Lee,* KAIST & IBS, Republic of Korea*; H. Choi,* Electronics and Telecommunications Research Institute (ETRI), Republic of Korea*; J.Y. Park,* Institute for Basic Science (IBS) & Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

Direct detection of hot electrons produced by exothermic reactions on catalysts is an effective strategy to quantify the non-adiabatic energy transfer during the elementary steps of the surface reactions, which provides an insight of the catalytic activity.[1,2] In particular, hot electron dynamics at the surface of metal nanoparticles (NPs) with precisely controlled shape and size is a challenge as well as a key issue in the real-world catalyst system. Herein, we show a novel scheme of graphene catalytic nanodiode composed of a Pt NPs array on graphene/TiO_2 Schottky nanodiode, which allows detection of hot electron flows induced by hydrogen oxidation on Pt NPs. By analyzing the correlation between the turnover rate (catalytic activity) and hot electron current (chemicurrent) measured on the graphene catalytic nanodiodes, we demonstrate that the catalytic nanodiodes utilizing a single graphene layer for electrical connection of Pt NPs are beneficial for the detection of hot electrons due to not only atomically thin nature of graphene but also reducing the height of the potential barrier existing at the Pt NPs/graphene interface. Thereby, the graphene catalytic nanodiodes offer an effective and easy to use approach to study mechanisms of chemical energy conversion in various heterogeneous system, even including composite catalysts with carbon-based supports.

References

1. H. Lee, I. I. Nedrygailov, Y. K. Lee, C. Lee, H. Choi, J. S. Choi, C. Choi, J. Y. Park, Nano Lett. 16 (2016) 1650-1656.

2. H. Lee, I. I. Nedrygailov, C. Lee, G. A. Somorjai, J. Y. Park, Angew. Chem. Int. Ed. 54 (2015) 2340-2344.

8:20am **SS1+AS+HC+NS-TuM2 Adlayer-Structure Dependent Ultrafast Desorption Dynamics: The Coverage Dependence of Substrate–Adsorbate Energy Transfer in Carbon Monoxide on Pd(111)***, **Sung-Young Hong**,* Brookhaven National Laboratory*; P. Xu,* Stony Brook University*; N.R. Camillone, M.G. White, N. Camillone,* Brookhaven National Laboratory

We have conducted a detailed investigation of the coverage dependence of the ultrafast photoinduced desorption of CO from the (111) surface of palladium. Because the CO binding site depends on coverage, these measurements present an opportunity to examine the dependence of the substrate–adsorbate energy transfer on adsorption site. Specifically, as the CO coverage is increased, the adsorption site population shifts from all three-fold hollow (up to 0.33 ML), to bridge and near bridge (> 0.5–0.6 ML) and finally to mixed three-fold hollow plus top site (0.6 ML to saturation at 0.75 ML). We show that between 0.24 and 0.75 ML this progression of binding site motifs is accompanied by two remarkable features in the ultrafast photoinduced desorption of the adsorbates: (i) a roughly two-orders of magnitude increase in the desorption probability, and (ii) a nonmonotonic variation in the adsorbate–substrate energy transfer rate observed in two-pulse correlation experiments, with a minimum occurring at intermediate coverages. Simulations using a phenomenological model to describe the adsorbate–substrate energy transfer in terms of frictional coupling indicate that these features are consistent with an adsorption-site dependent electron-mediated energy coupling strength, η_{el}, that decreases with binding site in the order: three-fold hollow > bridge and near bridge > top site. The weakening of η_{el} largely counterbalances the decrease in the desorption activation energy that accompanies this progression of adsorption site motifs and moderates what would otherwise be a rise of several orders of magnitude in the desorption probability. Furthermore, we show that within this framework, the observed energy transfer rate enhancement at saturation coverage is due to interadsorbate energy transfer from the copopulation of molecules bound in three-fold hollows to their top-site neighbors. This conclusion is supported by comparison to desorption of CO from mixed CO+O adlayers where the O adsorbs at three-fold hollow sites and further promotes CO desorption from top sites.

8:40am **SS1+AS+HC+NS-TuM3 Evidence for a Spin Accelerated Reaction Mechanism in the Thermal Decomposition of Alkyl Radicals on the Si(100) Surface***, A.J. Pohlman, D.S. Kaliakin, S.A. Varganov,* ***Sean Casey**,* University of Nevada

Density functional theory and complete active space self-consistent field calculations were used to probe the thermal decomposition of alkyl radicals on the Si(100) surface. Single dimer and single row double dimer cluster models were used to mimic the Si(100) surface in the calculations, and results indicate an interdimer β-hydrogen elimination reaction is the kinetically favored thermal decomposition pathway for adsorbed alkyl radicals. This pathway occurs via a spin crossing from the initial singlet energy surface to the triplet surface mediated by spin-orbit coupling. On the triplet surface the barrier to the elimination reaction is predicted to be about 40 kJ/mol lower than on the singlet surface. Experimental thermal desorption studies of alkyl chlorides adsorbed onto the Si(100)-(2x1) surface appear to give desorption energies for alkene products that are consistent with the barriers computed for the interdimer β-hydrogen elimination spin accelerated reaction mechanism. Experimental and computational results for the adsorption/desorption energetics of several different alkyl radicals will be discussed, along with results from partial deuteration studies of adsorption of selected haloalkanes.

9:00am **SS1+AS+HC+NS-TuM4 Hyperthermal Ion Induced Hot Carrier Excitations in a Metal Probed using Schottky Diodes***, **Dhruva Kulkarni**, D.A. Field, D.B. Cutshall, J.E. Harriss, W.R. Harrell, C.E. Sosolik,* Clemson University

We present measurements on hot carrier excitations in a metal irradiated by hyperthermal energy ions.

Specifically, alkali (Na^+/Rb^+) and noble gas(Ar^{q+}) ions were used to irradiate a Schottky diode consisting of

a thin film of Ag (~25nm) grown on an n-type Si (111) wafer. Measurements of the resultant current

through the device were performed as a function of energy, angle of incidence and velocity of the

incident ions. Energy loss of the incident energetic ions inside the metal film leads to the generation of

hot carriers that travel ballistically to the Schottky interface and are detected as a kinetically-induced

current or “kinecurrent” within the device. This kinecurrent is analogous to previous measurements of

“chemicurrent” [H. Nienhaus, *Surface Science*, **45**, 1-78 (2002)], which were linked to the energy

delivered to a surface by exothermic reactions that could non-adiabatically couple to the electronic

structure and generate hot carriers.

9:20am **SS1+AS+HC+NS-TuM5 H Atom Scattering, Adsorption, and Absorption in Collisions with Metal Surfaces: the crucial role of electron-hole-pair excitation***, M. Alducin,* Donostia International Physics Center, Spain*;* ***Daniel Auerbach**,* Max Planck Institute for Biophysical Chemistry, Germany*; M. Blanco-Rey,* Donostia International Physics Center, Spain*; O. Bünermann, Y. Dorenkamp,* Georg-August University of Göttingen*; S.M. Janke,* Max Planck Institute for Biophysical Chemistry, Germany*; H. Jiang,* Georg-August University of Göttingen*; A. Kandratsenka,* Max Planck Institute for Biophysical Chemistry*; G-J. Kroes,* Leiden Institute of Chemistry, The Netherlands*; M. Kammler,* Max Planck Institute for Biophysical Chemistry*; M. Pavenelo,* Leiden Institute of Chemistry **INVITED**

When an H atom collides with a solid surface, it can transfer some of its kinetic energy into elementary excitations of the solid like phonons and electron-hole pairs. If the atom loses enough kinetic energy, it can become bound to the solid, either on the surface or in the bulk. For a metal, the availability of a continuum of low lying electronic excitations can lead to the breakdown of the adiabatic Born Oppenheimer approximation and the facile nonadiabatic excitation of electron-hole pairs (ehp). If the H atom loses sufficient energy, it can enter a bound state with the solid, either on the surface or in the bulk.

We have used a combined theoretical and experimental approach to elucidate the relative roles of adiabatic processes (phonon excitation) and

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[*] **National Student Award Finalist**

nonadiabatic processes (ehp excitation) in collisions of H atoms with metals, insulators, and graphene. The experiments use photolysis to produce nearly mono-energetic beams of H atoms with energies of 1 - 3.3 eV and high resolution energy loss measurements using Rydberg atom tagging time-of-flight analysis. The theory involves calculations of classical trajectories for H atom collisions with two techniques. In the first, we calculate energies and forces on-the-fly during the course of a trajectory using density functional theory (DFT) and ab initio molecular dynamics (AIMD). In the second, we construct a full dimensional potential energy surface (PES) using a flexible functional form fit to DFT energies and bulk properties of the solid.

The measured mean energy loss for H atoms scattering from metals is large, approximately 30% of the initial energy and there is a tail in the energy loss distribution (ELD) extending to the full energy of incidence. The measured ELD is in reasonable agreement with theory only if nonadiabatic effects are included; adiabatic theory drastically underestimates the energy loss. Scattering from insulators (where ehp excitation can be excluded) shows much smaller energy loss and results consistent with adiabatic theory.

For metals, nonadiabatic effects not only dominate the energy loss process, but also change both the magnitude and mechanism for adsorption on metals. With nonadiabatic effects, the most probable pathway to adsorption is for H atoms to penetrate the surface, lose energy in the subsurface region, and then reemerge to adsorb on the surface.

11:00am **SS1+AS+HC+NS-TuM10 Progress in Characterizing Submonolayer Island Growth: Capture-Zone Distributions, Growth Exponents, and Transient Mobility***, **Theodore L. Einstein,*** University of Maryland, College Park*; A. Pimpinelli,* Rice University*; J.R. Morales-Cifuentes,* Unversity of Maryland, College Park*; D.L. González,* Universidad del Valle, Colombia

Analyzing capture-zone distributions (CZD) using the generalized Wigner distribution (GWD) has proved a powerful way to gain insight into epitaxial growth, in particular to access the critical nucleus size *i*, as reviewed in [1]. The CZ of an island contains all points closer to that island than to any other and is known as a Voronoi tesselation. This approach complements measurements of the growth exponent α from the scaling (with flux *F*) of island density $N \sim F^{\alpha}$ and of the distribution of island sizes. We summarize some extensive Monte Carlo simulations and experiments, especially newer ones, on various systems to which the GWD has been applied. These experiments include atomic or organic adsorbates, sometimes with impurities, and colloidal nano-particles. In some cases, most notably parahexaphenyl (6P) on sputter-modified mica [2], the value *i* extracted from CZD) differs from the [larger] values of *i* deduced from $N \sim F^{\alpha}$. Furthermore, while the scaling was good, the values of α differed considerably at small and large *F*, which was attributed to DLA and ALA dynamics [2]. To reconcile the CZD and scaling measurements, we took into account long-known transient mobility (hot precursors) using a rate-equation approach [3]. We also applied this method to data for pentacene (5A) on the same substrate. In applications of the GWD to social phenomena, notably the areas of secondary administrative units (e.g. counties or French *arrondissements*) [4], lognormal distributions (typically due to multiplicative noise) sometimes arise instead of GWD or gamma distributions; we show this also occurs for some pore-size distributions [5].

*Work at UMD supported by NSF CHE 13-05892

[1] T.L. Einstein, A. Pimpinelli, D.L. González, J. Cryst. Growth **401** (2014) 627; TLE, AP, DLG, J.R. Morales-Cifuentes, J. Physics: Conf. Ser. J. Phys.: Conf. Series **640** (2015) 012024

[2] T. Potocar et al., Phys. Rev. B **83** (2011) 075423 & later work by A. Winkler et al., see [1].

[3] JRM-C, TLE, and AP, Phys. Rev. Lett. **113** (2014) 246101.

[4] R. Sathiyanarayanan, Ph.D. thesis, UMD, 2009; R. Sathiyanarayanan and TLE, preprint.

[5] A.S. DeLoach, B.R. Conrad, TLE, and D.B. Dougherty, submitted.

11:20am **SS1+AS+HC+NS-TuM11 Hindered Translator and Hindered Rotor Models for Calculating the Entropy of Adsorbed Species***, **Lynza H. Sprowl**[*],* Oregon State University*; C.T. Campbell,* University of Washington*; L. Arnadottir,* Oregon State University

Adsorbed species on surfaces are important for a range of applications including heterogeneous catalysis, corrosion processes, and film growth. The need for a fast and accurate way to predict equilibrium constants and rate constants for surface reactions is important for understanding reaction kinetics and for building microkinetic models of catalytic reactions. Here a method to calculate partition functions and entropy of adsorbed species is presented. Instead of using the vibrational frequencies estimated from density functional theory and the harmonic oscillator approximation to calculate the partition function for all modes of motion, we use hindered translator and hindered rotor models for the three modes of motion parallel to the surface, two translations and one rotation. The energy barriers for translation and rotation were determined using density functional theory and the nudged elastic band method for four different adsorbates on a platinum surface: methanol, propane, ethane, and methane. The hindered translator model was used to calculate the entropy contributions from the two translations parallel to the surface and the hindered rotor model was used to calculate the entropy contribution from the rotation about the axis perpendicular to the surface. When combined with the vibrational entropy contributions and the concentration related entropy contributions, this gives the total entropy of the adsorbate on the surface. The total adsorbate entropies were found to agree well with experimental results, with an average absolute value of the error of only 1.1R or 8% for the four adsorbates. This new model should be useful to future researchers in surface chemistry, since it provides more accurate predictions of standard-state entropies and partition functions, and thus more accurate equilibrium constants and rate constants for surface reactions than provided by the standard harmonic oscillator approximation.

11:40am **SS1+AS+HC+NS-TuM12 Stabilization of *X*-Au-*X* Complexes on the Au(111) Surface: A Theoretical Investigation and Comparison of *X*=Sulfur, Chlorine, Methythiolate, and Silylthiolate***, J. Lee, J.S. Boschen, T.L. Windus, P.A. Thiel, J.W. Evans,* ***Da-Jiang Liu,*** Iowa State University

The involvement of Au atoms in the self-assembled methylthiolate (CH_3S) monolayers on Au(111) has been demonstrated experimentally [1], while for S and Cl, chain-like structures with no direct Au involvement were found [2,3]. We find that for S on various coinage metal surfaces, the linear S-M-S complexes (M=Cu, Ag, Au) are prevalent. A systematical theoretical study of the X-Au-X complexes, with X=S, Cl, CH_3S, and SiH_3S, has been performed using DFT and other quantum chemistry methods. Assuming equilibration of the metal substrate, the chemical potential of X are calculated and used to predict the stability of various Au-X complexes. We find good agreement between DFT and available experimental findings. Furthermore, the van del Waals interaction is shown to play a crucial role in the self-assembly of CH_3S observed in experiments [1].

[1] P. Maksymovych, O. Voznyy, D. B. Dougherty, D. C. Sorescu, J. T. Yates Jr., *Prog. Surf. Sci.***85**, 206 (2010).

[2] V. V. Zheltov *et al.Phys. Rev. B,* **89**, 195425 (2014).

[3] H. Walen, *J. Chem. Phys.***143**, 014704 (2015).

12:00pm **SS1+AS+HC+NS-TuM13 Contrasting Phonon Confinement and Interface Stability at Fe-Ag and Fe-Cr Multilayers: Insights from *Ab Initio* Calculations***, S. Hong,* ***Talat Rahman,*** University of Central Florida

We have performed density functional theory based calculations to compare the characteristics of the interface of Fe-Ag and Fe-Cr multilayers. A perfect interface lattice match between the Fe and Ag layers was obtained by rotating fcc Ag(100) layers by 45° on bcc Fe(100). On the other hand, the Fe-Cr interface could be modeled by epitaxial layers of bcc Fe(100) and Cr(100). In Fe-Ag multilayers, we find the signature peak of Fe bulk phonons (35 meV) to be completely diminished, while the low energy peaks are remarkably enhanced, in agreement with experiment [1]. In contrast, the phonon density of state in the Fe-Cr multilayers do not show any salient feature except a slight decrease in the 35 meV peak for the Fe layer at the interface, as compared to that of the middle Fe layer, again in agreement with experiment [2]. The magnetic moment of the interfacial Fe atoms is larger than that of Fe atoms in other layers, as a result of charge transfer from Fe to Ag at the interface. As compared to the middle layers, more spin-up and less spin-down states are occupied at the interface in such a way that Fe donates a large number of spin-down electrons to Ag but receives only a few spin-up electrons from the latter because of the almost fully occupied Ag d-band. This leads to rather unstable Fe-Ag interface. On the contrary, at the Fe-Cr interface, Cr can easily give and take electrons leading to smooth interfacial coupling and stable environment.

[1] B. Roldan Cuenya et al., to be published

[2] Roldan et al, Phys. Rev. B 77, 165410 (2008).

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[*] **Morton S. Traum Award Finalist**

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