

# Wednesday Morning, November 12, 2014

## Surface Science

Room: 309 - Session SS+AS+EN-WeM

### Dynamic Processes of Single Atoms and Molecules at Surfaces

**Moderator:** Arthur Utz, Tufts University, Andrew Gellman, Carnegie Mellon University

8:00am SS+AS+EN-WeM1 **Construction and Manipulation of Individual Functional Molecules: from Reversible Conductance Transition to Reversible Spin Control**, *Hong-Jun Gao*, Chinese Academy of Science, China **INVITED**

Control over charge and spin states at the single molecule level is crucial not only for a fundamental understanding of charge and spin interactions but also represents a prerequisite for development of molecular electronics and spintronics. While charge manipulation has been demonstrated by gas adsorption and atomic manipulation, the reversible control of a single spin of an atom or a molecule has been challenging. In this talk, I will present a demonstration about a robust and reversible spin control of single magnetic metal-phthalocyanine molecule via attachment and detachment of a hydrogen atom, with manifestation of switching of Kondo resonance. Low-temperature atomically resolved scanning tunneling microscopy was employed. Using density functional theory calculations, the spin control mechanism was revealed, by which the reduction of spin density is driven by charge redistribution within magnetic 3d orbitals rather than a change of the total number of electrons. This process allows spin manipulation at the single molecule level, even within a close-packed molecular array, without concern of molecular spin exchange interaction. This work opens up a new opportunity for quantum information recording and storage at the ultimate molecular limit.

References:

1. L. W. Liu, K. Yang, Y. H. Jiang et al., Scientific Report 3, 1210 (2013).
2. L. Gao et al., Phys. Rev. Lett. 99, 106402 (2007).

\*In collaboration with Liwei Liu, Kai Yang, Yuhang Jiang, Boqun Song, Wende Xiao, Linfei Li, Haitao Zhou, Yeliang Wang, and Shixuan Du, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

8:40am SS+AS+EN-WeM3 **Single Molecule Origins of Electronic Disorder: Random Conformations of  $\alpha$ -NPD Molecules on Au(111)**, *Daniel Dougherty, J. Wang, J. Wang*, North Carolina State University

Disorder is an important aspect of modeling organic and polymeric electronic materials. Proper accounting of the effects of disorder both in active layers and at interfaces with contacts determine the detailed current-voltage characteristics in organic thin film devices [1]. Our study seeks to visualize and statistically quantify the disorder in  $\alpha$ -NPD films at the single molecule scale. This molecule is a common hole transport material in organic LEDs and has been found to exhibit strong disorder in thin film diode geometries [2]. We used scanning tunneling microscopy and spectroscopy to observe numerous surface structures of  $\alpha$ -NPD on the (111) surface of Au. These structures are distinguished by different lateral order as well as different local molecular conformations. Random molecular conformations on the surface lead to an statistical distribution of hole transport states that is consistent with the distribution inferred from device analysis. \*This work was funded by an NSF CAREER award through DMR-1056861. [1] Tessler et al., Adv. Mater. 21, 2741 (2009) [2] van Mensfoort et al., J. Appl. Phys. 107, 113710 (2010)

9:00am SS+AS+EN-WeM4 **Pt-Cu Single Atom Alloys for the Selective Partial Hydrogenation of Butadiene**, *Felicia Lucci, M. Marcinkowski, E. C. H. Sykes*, Tufts University

Butene is a common feedstock for polymerization reactions; however, butadiene is a minority impurity that poisons the polymerization catalyst. The selective hydrogenation of butadiene to butene serves to increase the purity of the feedstock without reducing the overall concentration of butene. Therefore, catalysts that selectively hydrogenate butadiene to butene and prevent the hydrogenation of butene to butane are of great interest. Using scanning tunneling microscopy (STM) and temperature programmed desorption/reaction (TPD/R), we show that Pt-Cu single atom alloys catalyze hydrogenation of butadiene to butene with 100% selectivity. The addition of small amounts of Pt (~1%) into Cu reduces the barrier for H<sub>2</sub> dissociation, allowing for the low temperature dissociation of H<sub>2</sub>. H atoms spill-over onto the Cu sites increasing the concentration of weakly bound H atoms available for the hydrogenation reaction. The weakly bond H atoms

readily hydrogenate butadiene to butene. TPR of co-adsorbed H and butadiene shows the exclusive desorption of reactively formed butene, where the reaction extent is limited by the availability of H on the surface. While the individual, isolated Pt atoms in the Cu terrace activate molecular H<sub>2</sub>, they do not induce the decomposition of butadiene as observed on Pt(111) surfaces. The ability to control geometries of atomic ensembles and hence the extent of hydrogenation reactions using *single atom alloys* allows for the production of new and efficient catalysts.

9:20am SS+AS+EN-WeM5 **Toward a Dynamical Understanding of Chemistry at Metal Surfaces**, *Alec Wodtke*, Max Planck Institute for Biophysical Chemistry **INVITED**

One of our most fundamental scientific challenges is to develop predictive theories of chemistry rigorously grounded in the laws of physics. In 1929, Dirac identified the problem famously in a comment about the importance of quantum mechanics to chemistry... "*The underlying physical laws necessary for the mathematical theory of... the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.*" Despite electrifying advances in computational power, Dirac is still right. The theory of chemistry requires approximate methods for practical computations.

For the theory of surface chemistry, three central approximations are made, involving the use of: 1) classical mechanics for describing nuclear motion, 2) density functionals for calculating electronic states and the Born-Oppenheimer approximation to separate electronic and nuclear degrees of freedom.

The growing importance of computational surface chemistry motivates us to design rigorous experimental tests of these assumptions. Many fundamental questions arise. Can we trust the Born-Oppenheimer approximation for calculating potential energy surfaces for reactions at metal surfaces? Can we characterize and overcome the weaknesses of density functional theory, for example by developing new wave-function based methods for the solid-state? For all of these reasons, it is important to carefully design experimental tests of the capabilities of modern computational surface chemistry.

Using modern molecular beams methods in state-to-state scattering experiments, we obtain a wealth of observational data characterizing the interactions of molecules with metal surfaces. Emphasizing quantitative comparison to first principles theories, we find that energy conversion can occur by unexpected mechanisms, where the electronically adiabatic approximation separating the time scales of electronic and nuclear motion is found to be invalid. The simplicity of the systems under study provides opportunities for developing new theories that go beyond the Born-Oppenheimer approximation. One important outcome of this is the realization that Born-Oppenheimer breakdown can be induced by simple electron transfer events that are common in surface chemistry.

11:00am SS+AS+EN-WeM10 **Steric Effect in O<sub>2</sub> Chemisorption on Al(111)**, *Mitsunori Kurahashi, Y. Yamauchi*, National Institute for Materials Science (NIMS), Japan

O<sub>2</sub> adsorption on Al(111) has been investigated intensively as the most representative system of surface oxidation. The dynamical process happening on the surface, however, remained unclear. An STM study by Brune et al.[1] has proposed that adsorbed O-atoms are atomic and are well separated each other. Initially, this has been ascribed to the transient mobility driven by the O<sub>2</sub> chemisorption energy ("hot-atom" mechanism)[1], but this mechanism has been found to be unlikely. The abstraction mechanism, in which one O-atom is bound to the surface while the other is ejected, has been proposed alternatively based on the resonance enhanced multi-photon ionization measurement.[2] It is however not evident whether or not the abstraction process is the dominant event at low translational energies (E<sub>0</sub>). In addition, the STM study by Schmid et al.[3] has suggested that the adsorbates consist of two O-atoms locating at nearby sites. This cannot be explained by the abstraction mechanism.

In this study, we focused attention to the alignment dependence in the O<sub>2</sub> sticking to clarify the reaction mechanism. A single spin-rotational state-selected [(J,M)=(2,2)] O<sub>2</sub> beam, for which we can specify both the molecular alignment and spin direction relative to the magnetic field, was adsorbed on an Al(111) surface. The results show that O<sub>2</sub> molecules parallel to the surface have much higher sticking probabilities than those perpendicular to the surface at E<sub>0</sub> < 0.2 eV. The E<sub>0</sub> dependence of the sticking probability indicates that the dissociation barrier at the perpendicular geometry is about 0.1 eV higher than at the parallel geometry. The present results reveal that the abstraction process, which occurs at the perpendicular geometry, is a minor event at low E<sub>0</sub>. [4]

[1] Brune et al., Phys. Rev. Lett., 68, 624 (1992). [2] Komrowski et al., Phys. Rev. Lett., 87, 246103 (2001). [3] Schmid et al., Surf. Sci., 478, L355 (2001). [4] Kurahashi et al., Phys. Rev. Lett., 110, 246102 (2013)

11:20am **SS+AS+EN-WeM11 Surface Temperature Effects in Methane Dissociation on Ni and Ir Surfaces**, Arthur Utz, E. Peterson, E. Dombrowski, E. High, E. Nicotera, Tufts University

Recent transition state and quantum dynamics calculations have suggested an important role for surface atom motion in promoting methane dissociation on transition metals including Ni, Pt, and Ir. Here, we describe state-resolved gas-surface scattering measurement of methane dissociation on Ni(111), Ir(111), and Ir(110)-(1x2). Infrared laser excitation prepares methane in a single excited rotational and vibrational state with a precisely defined internal energy. A supersonic molecular beam provides tight control over the translational energy of the methane molecules. The methane molecules, with their well-defined energy, accentuate the role of surface temperature, and the resulting thermal motion of surface atoms, on reactivity.

The presentation will focus on recent experimental results. On the Ir(110)-(1x2) surface, we observe both precursor-mediated and direct reaction channels for the vibrationally excited ( $v_3$ ,  $v=1$ ) molecules at surface temperatures of 300K or higher. For  $v=0$  molecules, a precursor-mediated pathway appears for surface temperatures above 500K, but not for temperatures of 500K or lower. The abrupt disappearance of the precursor-mediated reaction path correlates with a surface reconstruction to (331) facets that was previously reported to occur at 500K. We will report on measurements that extend the temperature range for the vibrationally excited ( $v_3$ ,  $v=1$ ) molecules to temperatures between 100 and 300K on the Ir(110) surface. We will also report on more recent studies that explore the surface temperature dependence of more highly vibrationally excited methane molecules.

11:40am **SS+AS+EN-WeM12 Activation of C<sub>1</sub>-C<sub>9</sub> Alkanes on Pt(111): Importance of Dynamics, van der Waals Interactions, and Gas-Surface Energy Transfer**, Jason Navin, S.B. Donald, G. Cushing, I.A. Harrison, University of Virginia

A variety of dissociative sticking coefficients (DSCs) were measured for alkanes varying in size from methane to nonane on Pt(111) using an effusive molecular beam technique. Thermal equilibrium ( $T_g = T_s$ ) and non-equilibrium ( $T_g \neq T_s$ ) DSC measurements provided information about the gas-surface reactivity and energy transfer. Angle-resolved DSCs,  $S(700\text{ K}; \theta)$ , measured for methane, ethane, and propane on Pt(111) were used to define thermal DSCs,  $S(T)$ , and discern dynamical behavior. Methane and ethane DSCs were sharply peaked around the surface normal and were found to have similar dynamical biases away from statistical behavior. Precursor-mediated microcanonical trapping (PMMT) models were used to both analyze and predict DSCs over a wide range of experimental conditions and experiments. It was found that the activation energy for dissociative chemisorption of an alkane scales linearly with its molecular desorption energy from the physisorption well in front of the surface. The molecular desorption energy should be proportional to the van der Waals stabilization energy for the products of dissociative chemisorption. The gas-surface energy transfer increased as the alkane size increased from C<sub>1</sub> to C<sub>9</sub>. For alkanes larger than C<sub>4</sub>, the gas-surface energy transfer was apparently sufficient to fully thermalize the impinging molecule to the temperature of the surface before reaction such that,  $S(T_g=300\text{K}, T_s) = S(T)$ .

12:00pm **SS+AS+EN-WeM13 Shining light on an Important Intermediate Step in Photocatalysis: Probing Polarons in ZnO using Infrared Reflection Absorption Spectroscopy**, Fabian Bebensee, H. Sezen, Karlsruhe Institute of Technology, Germany, A. Nefedov, C. Wöll, Karlsruhe Institute of Technology

ZnO is a wide-bandgap metal oxide exhibiting various highly desirable physico-chemical properties, among them high photocatalytic activity. As such, it has been widely studied employing virtually all available techniques over the past 50 years.<sup>[1]</sup> In the context of photoexcitations, primarily excitons have been studied extensively including their very recently reported ultrafast formation dynamics.<sup>[2]</sup> In photocatalysis, dissociation of excitons into free electrons and holes takes place and therefore the binding energies of the polaronic states become crucial for the subsequent steps on the way to finally transferring an electron or hole onto an adsorbed molecule. Despite their importance in photochemistry (see recent work on TiO<sub>2</sub><sup>[3]</sup>), very little work has been devoted to these trap states in ZnO. Here, we report a novel approach to study polarons in ZnO single crystal substrates: the polaron traps are populated via UV-light irradiation and then probed using infrared reflection absorption spectroscopy (IRRAS). Upon irradiation, a number of previously unobserved, well-defined and sharp absorption bands appear in the IR-spectra. Among these new features is an absorption-edge like feature that we assign to excitations of electrons from

the conduction band into hole polaronic trap states. From their time-dependent intensity, we infer a (temperature-dependent) life time of 25 seconds at 75 K. The implications of these findings for ZnO photochemistry will be discussed.

[1] C. Klingshirn, *physica status solidi (b)* **2007**, 244, 3027-3073.

[2] J.-C. Deinert, D. Wegkamp, M. Meyer, C. Richter, M. Wolf, J. Stähler, *Physical Review Letters* **2014**, 113, 057602.

[3] H. Sezen, M. Buchholz, A. Nefedov, C. Natzeck, S. Heissler, C. Di Valentin, C. Wöll, *Sci Rep-Uk* **2014**, 4, 3808.

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