

# Monday Afternoon, October 15, 2007

## Surface Science

Room: 611 - Session SS2-MoA

## Electronic and Vibrational Structure

Moderator: M. Trenary, University of Illinois at Chicago

2:00pm **SS2-MoA1 Action Spectroscopy of Single Adsorbate Motions, H. Ueba**, The University of Toyama, Japan **INVITED**

I will discuss an idea of action spectroscopy for a single molecule motion induced by vibrational excitation with a scanning tunneling microscope (STM).<sup>1</sup> A simple formula describing the energy transfer from the vibrational mode excited by tunneling electrons to a reaction coordinate mode through anharmonic coupling to overcome the activation barrier<sup>2,3</sup> is combined with the inelastic tunneling current calculated using the non-equilibrium Keldysh Green's function method. This enables the reaction rate to be calculated as a function of the bias voltage, and is applied to CO hopping on Pd (110)<sup>2</sup> and CCH rotation on Cu(001).<sup>4</sup> I propose that the second-derivative of the reaction rate with respect to the bias voltage gives the density of states of the vibrational mode excited by tunneling electrons,<sup>4</sup> which can not be directly observed with inelastic tunneling spectroscopy because of the negative contribution of the elastic current to the total current, and when a molecule motion is induced by the vibrational excitation.

<sup>1</sup>H. Ueba, B.N.J. Persson, Phys. Rev. B 75, 041403(R) (2007).

<sup>2</sup>T. Komeda et al., Science 255, 2055 (2002).

<sup>3</sup>B.N.J. Persson, H. Ueba, Surf. Sci. 502/503, 18 (2002).

<sup>4</sup>L.J. Lauhon, W. Ho, Surf. Sci. 451, 219 (2000).

2:40pm **SS2-MoA3 Action Spectroscopy of vibrationally excited molecules by inelastically tunneled electrons, Y. Kim**, RIKEN, Japan

The excitation of molecular vibration by means of the inelastically tunneled electrons from the tip of a scanning tunneling microscope (STM) can lead to various dynamical processes at surfaces.<sup>1-5</sup> The vibrational spectrum of a single molecule provides useful information not only for the chemical identification of the molecule but also for investigating how molecular vibration can couple with the relevant dynamical processes. Inelastic electron tunneling spectroscopy with the STM (STM-IETS) has been mainly used for obtaining vibrational spectrum of individual molecules. STM-IETS detects the vibrational modes of a single molecule by measuring the total conductance change resulting from both elastic and inelastic electron tunneling.<sup>2,3</sup> However, the STM-IETS is not applicable to some molecules showing mobile character when they are vibrationally excited by inelastically tunneled electrons during measurement. The response of vibrationally mediated molecular motion to applied bias voltage, namely an "action spectrum", can reveal vibrational modes that are not visible in STM-IETS, because the molecular motion is induced via only inelastic tunneling.<sup>3,5</sup> Thus, the action spectrum would be a candidate for detecting which vibrational mode is actually excited and associated with molecular motions. Here, I discuss the usefulness and selection rules of the two types of single molecule vibrational spectroscopic methods by considering the action spectroscopy as an alternative vibrational spectroscopic method for the STM-IETS through the study of vibrationally mediated molecular motions with a low-temperature STM.

<sup>1</sup>T. Komeda, Y. Kim, M. Kawai, B.N.J. Persson, H. Ueba: Science 295 (2002) 2055.

<sup>2</sup>Y. Kim, T. Komeda, M. Kawai: Phys. Rev. Lett. 89 (2002) 126104.

<sup>3</sup>Y. Sainoo, Y. Kim, T. Okawa, T. Komeda, H. Shigekawa, M. Kawai: Phys. Rev. Lett. 95 (2005) 246102.

<sup>4</sup>M. Ohara, Y. Kim, M. Kawai: Chem. Phys. Lett. 426 (2006) 357.

<sup>5</sup>M. Ohara, Y. Kim, M. Kawai: Jpn. J. Appl. Phys. Part 1 45 (2006) 2022.

3:00pm **SS2-MoA4 "Walking" Molecules and their Dynamics and Energetics, K.L. Wong, G. Pawin, D.H. Kim, L. Bartels**, University of California, Riverside

Thiol groups, despite being proposed as rigid linker for many molecular electronics applications, anchor aromatic molecules to metal surfaces in a fashion that permits rapid rearrangement of the molecule on the substrate even at temperatures as low as 60K. The aromatic ring of individual benzenethiol molecules experiences a rotation barrier around the substrate linker of ca. 120 meV; even diffusion of the sulfur anchor on the substrate has a barrier of only ca. 150 meV.<sup>1</sup> Placement of two thiol groups in a molecule (9,10-dithionanthracene, DTA) does not increase the diffusion barrier. Rather it renders the molecule's diffusion behaviour on Cu(111) anisotropic, i.e. following a single line on the otherwise threefold symmetric substrate.<sup>2</sup> Density functional theory calculations show, that this behaviour

originates from sequential occupation of optimal adsites by each of the two substrate linkers, strikingly resembling bipedal locomotion ("walking"). The resultant linear (uniaxial) motion on the surface can be used for transport of "cargo" molecules across a surface<sup>3</sup> as well as for the exploration of fundamental concepts of chemistry.

<sup>1</sup>K.L. Wong et al., Appl. Phys. Lett. 88, 183106 (2006)

<sup>2</sup>K.-Y. Kwon et al., Phys. Rev. Lett. 95, 166101 (2005)

<sup>3</sup>K.L. Wong et al., Science 315, 1391 (2007)

3:40pm **SS2-MoA6 Feedback-Controlled Single Molecule Surface Chemistry, N.L. Yoder, J.S. Fakanas, M.C. Hersam**, Northwestern University

In the past 25 years, the scanning tunneling microscope (STM) has enabled the detailed study of the chemistry and physics of single molecules on surfaces. Electron-driven processes (including desorption and dissociation) are especially advantageous because they offer the possibility of rapidly exciting a molecule far from equilibrium with exceptional spatial localization of the excitation.<sup>1</sup> Attaining precise control over the electron dose requires a method for both detecting the desired events and rapidly terminating the flow of electrons to prevent overdosing. A significant advance in this area was Feedback Controlled Lithography (FCL),<sup>2</sup> which involved the creation of isolated reactive sites on H:Si(100) through the controlled desorption of hydrogen. Since reaction products could also be susceptible to electrons, the ability to both detect a molecular conformational change and immediately terminate the flow of electrons is fundamentally relevant to the study of single-molecule processes. In this study, we apply this technique to the investigation of the byproducts of cyclopentene desorption<sup>3</sup> from clean Si(100). Experiments were performed using a cryogenic ultra-high vacuum (UHV) STM operating at 8 K and 80 K. At low temperatures, cyclopentene molecules are controllably desorbed, and a feedback loop is utilized to detect the desorption event and halt electron flow. At the desorption conditions of -4 V and 2 nA, the desorption reaction alternately results in three distinct surface features: a clean silicon dimer (55 %), a half-dimer dark feature (30 %), and fully darkened silicon dimer (15 %). Additionally, the radial and angular distributions of the byproduct binding sites were also measured. The desorption products were often observed at significant distances from the initial desorption site, with some features as far as 3 dimer rows (~23 Å) away. The dark desorption products are attributed to hydrogen-passivated silicon atoms resulting from the dissociation of a cyclopentene C-H bond and the subsequent bonding of the ejected hydrogen with the reactive silicon surface. Finally, tunneling electrons from the STM tip were used to induce hopping and desorption of hydrogen from the partially passivated silicon dimers.

<sup>1</sup>A. J. Mayne et al., Chemical Reviews 106, 4355 (2006).

<sup>2</sup>M. C. Hersam et al., Nanotechnology 11, 70 (2000).

<sup>3</sup>N. L. Yoder et al., Physical Review Letters 97, 187601 (2006).

4:00pm **SS2-MoA7 Isotope-Specific Deposition of vibrationally excited molecules, D.R. Killelea, V.L. Campbell, N.S. Shuman, A.L. Utz**, Tufts University

Direct IR excitation of gas-phase reagents offers a potential means of isotope selective chemical vapor deposition (CVD). A narrow bandwidth IR laser selectively excites a vibrational mode in a single isotopomer of methane. These vibrationally excited molecules are significantly more reactive, enhancing their rate of deposition. Here we present results showing control of the carbon isotopic ratio of surface adsorbates by IR excitation of methane. We recombinatively desorb the methyl fragment deposited on a Ni(111) surface after methane dissociatively adsorbs on the surface. We are able to quantify the yield of both carbon-13 and carbon-12 using a mass spectrometer to measure <sup>13</sup>CH<sub>4</sub> and <sup>12</sup>CH<sub>4</sub> desorbing from the surface. Using a methane molecular beam with the natural abundance of carbon-13 and carbon-12, we are able to achieve an eight-fold enhancement in carbon-13 deposition by exciting less than 0.1% of the methane molecules in the molecular beam.

4:20pm **SS2-MoA8 Ion Effects on the Liquid-Vapor Interface of a Non-Aqueous Solution, M.J. Krisch, J.C. Hemminger**, University of California, Irvine, S. Baldelli, University of Houston

We find that electrolytes modify the liquid-vapor interface of a non-aqueous solution. A variety of recent studies have observed ion-dependent changes in the surface structure of aqueous electrolyte solutions. In this project, we examine the influence of the solvent by probing the surface structure of non-aqueous electrolyte solutions. Our experiments use surface-specific sum frequency vibrational spectroscopy to obtain information about the liquid-vapor interface. We examine a series of alkali halides in ethylene glycol in which the identity of the anion is varied systematically. The spectra show that the addition of salt modifies solution surfaces to a degree

that follows the polarizability of the anion in solution, particularly as seen through changes in the OH bonding stretch. Results are compared to surface tension measurements of the same solutions.

4:40pm **SS2-MoA9 Transport Limitations in Tunneling Spectroscopy of Pentacene on SiC**, *S. Gaan, R. Duca, R. Feenstra*, Carnegie Mellon University

Pentacene (Pn) is a promising material for organic field effect transistors because of its relatively high mobility and its tendency to form ordered structures. In this work we have used scanning tunneling microscopy (STM) and spectroscopy (STS) to probe the electronic properties of Pn thin films. The substrates were hydrogen-etched SiC, oxidized by exposure to 4000 L of molecular oxygen at 700°C. The Pn was deposited from a crucible by vacuum sublimation, with the sample at room temperature. On a large scale, the Pn films display a layered morphology with dendritic edges, consistent with prior results.<sup>1</sup> Within each layer, the molecules form ordered arrangements; it is on these regions that STS was performed. We obtain a HOMO-LUMO gap of about 2 eV.<sup>2</sup> Effects of degradation of Pn molecules were seen in the spectra, producing smearing of the band edges. Using the STM, with various tip-sample separations, widely different currents were injected into the sample in order to probe transport of the charge carriers. The tunnel current was found to saturate at positive bias for all tip sample separations, thus revealing a spreading resistance type of effect in Pn films. In other words, a quasi Fermi level exists in the sample and varies as a function of distance from the apex of the probe tip. In order to determine current saturation at negative bias, we examined the dependence of the current on tip-sample separation, at constant voltage. Significant deviation from ideal vacuum tunneling was observed, which also indicates transport limited tunnel current. To explain the observed transport limitation in the tunnel current we propose a simple two resistor model, one resistor for the vacuum and one for the sample, with the assumption that the sample resistance is constant. With different injection levels and voltages we obtain reasonable fits to the data. Using this model we are able to deduce resistivities of the sample for both filled and empty states,  $3.3 \times 10^2$  and  $2 \times 10^4 \Omega \text{ cm}$ , respectively. Work is underway to interpret these results in terms of possible transport mechanisms in our Pn thin films.

<sup>1</sup>Heringdorf et. al., Nature, 412, 517 (2001).

<sup>2</sup>Repp et. al., Phys. Rev. Lett., 94, 026803 (2005).

5:00pm **SS2-MoA10 Intrinsic Accumulation Layer Quantum Well States and Anomalous Valence Band Dispersion in Indium Nitride**, *K.E. Smith, L. Colakerol, T. Learmonth, P.A. Glans, L.F.J. Piper*, Boston University, *A. Fedorov*, Lawrence Berkeley National Laboratory, *T.D. Veal, C.F. McConville*, University of Warwick, UK, *S. Healy, E.P. O'Reilly*, University College Cork, Ireland, *T.C. Chen, T.D. Moustakas*, Boston University

The valence and conduction band electronic structure in InN thin films has been measured using high resolution Angle Resolved Photoemission Spectroscopy (ARPES). InN exhibits an accumulation layer near the film surface, and our ARPES measurements reveal that the conduction band electrons in the accumulation layer exist in intrinsic quantum well states.<sup>1</sup> We also used ARPES to measure the Fermi surface of these quantum well states, as well as their constant binding energy contours below the Fermi level. The energy of the Fermi level, and the size of the Fermi surface for these quantum well states could be controlled by varying the method of surface preparation. Furthermore, a minimum is observed in the dispersion of the top of the valence band, with the highest measured valence band having an electron-like dispersion at the Brillouin zone center, which is unexpected in the context of earlier measurements and calculations. Valence band holes see a quantum barrier near the surface, and a theoretical analysis using a k.p approach of the influence of this barrier indicates that the anomalous dispersion is most likely due to a negative crystal field splitting in InN, contrary to previous expectations. This work was supported in part by the DOE under RF-06-PRD-001 (subcontract from University of Nevada, Las Vegas), by the NSF under grant number DMR-0311792, and by Science Foundation Ireland. The ALS is supported by the DOE, Materials Sciences Division under contract no. DE-AC03-76SF00098.

<sup>1</sup> I. L. Colakerol, T.D. Veal, H.-K. Jeong, L. Plukinski, A. DeMasi, S. Wang, Y. Zhang, L.F.J. Piper, P.H. Jefferson, A. Fedorov, T.C. Chen, T. D. Moustakas, C.F. McConville, and K.E. Smith, Phys. Rev. Lett. 97, 237601 (2006).

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