

Wednesday Afternoon, November 11, 2009

Surface Science

Room: N - Session SS2-WeA

Surface Physics, Single Particle Imaging

Moderator: M. Trenary, University of Illinois at Chicago

2:00pm **SS2-WeA1 Dynamics of Alkali Metals Adsorbed on Cu(111) at Low Density using High Resolution ³He Spin-Echo Spectroscopy.** D.J. Ward, A.P. Jardine, H.J. Hedgeland, W. Allison, J. Ellis, University of Cambridge, UK

Alkali atoms at surfaces show unexpected behaviour arising from the strong interadsorbate forces and coupling of electronic and nuclear motion [2,3]. In the present work we present new results giving additional insight into both the dynamics and the scattering.

High resolution quasielastic helium atom scattering (QHAS) experiments provide a unique tool to study adsorbate dynamics[1] since ³He spin-echo measurements give the surface correlation in time through the intermediate scattering function (ISF), $I(\Delta K, t)$. The functional form of the ISF has a well defined analytic form for simple systems, however for real systems the form is typically complex and challenging to predict. For example the shape of the ISF can take a multifunctional form due to summation effects from multiple species or clusters moving with the same or different modes, and a convolution effect from differences in the local appearance of the potential energy landscape to the adsorbate for the length scale under study.

Previous investigations of the diffusion of alkali metals on metal surfaces have revealed unexpected phenomena. For sodium on Cu(100), a 'new' mode of aperiodic motion, perpendicular to the surface, was discovered[2]. For caesium, the observed dynamics on the same surface were found to be qualitatively different to sodium[3], indicating a critical balance of adsorbate-substrate and adsorbate-adsorbate interactions, determining the behaviour for each adsorbate.

In this work we present detailed helium-3 spin-echo QHAS measurements of the dynamics of sodium adsorbed on Cu(111) at low to moderate coverages. We observe a QHAS broadening with the presence of a complex lineshape which shows a momentum transfer variation. The functional form is compared with theoretical models[4] for different potential energy landscapes. The variation of the QHAS broadening with temperature and momentum transfer are studied to access information on the dynamic phenomena on the Cu(111) surface, exploring in particular the generality of perpendicular motion, and changes in the adsorbate-substrate/adsorbate-adsorbate force balance.

[1] A.P. Jardine, S. Dworski, P. Fouquet, G. Alexandrowicz, D. J. Riley, G. Y. H. Lee, J. Ellis, W. Allison, *Science* 304, 1790 (2004).

[2] G. Alexandrowicz, A. P. Jardine, H. Hedgeland, W. Allison, J. Ellis, *Phys. Rev. Lett* 97, 156103 (2006)

[3] A P Jardine, G Alexandrowicz, H Hedgeland, R D Diehl, W Allison and J Ellis, *J. Phys.: Cond. Matter* 19 305010 (2007)

[4] R. Martinez-Casado, J.L. Vega, A.S Sanz, S. Miret-Artes, *J. Chem. Phys.* 126, 194711-5 (2007)

2:20pm **SS2-WeA2 MORTON S. TRAUM AWARD FINALIST: Direct Observation of Hydrogen-Bond Exchange within a Single Water Dimer.** T. Kumagai*, M. Kaizu, H. Okuyama, Kyoto University, Japan, S. Hatta, T. Aruga, Kyoto University, JST-CREST, Japan, I. Hamada, Y. Morikawa, Osaka University, Japan

The nature of the hydrogen bond is related to many physical, chemical and biological processes. The structure and dynamics of water dimers, which consist of hydrogen-bond donor and acceptor molecules, have been subjects of extensive research as a prototype of much more complex hydrogen-bonding systems. The water molecules in a free water dimer rearrange the hydrogen bond through quantum tunneling among equivalent structures [1]. Recently, we reported the visualization in real space of hydrogen-bond exchange process governed by quantum tunneling within a single water dimer adsorbed on a metal surface with a low-temperature scanning tunneling microscope (STM) [2].

The experiments were carried out in an ultrahigh vacuum chamber equipped with STM operating at 6 K. The Cu(110) was cleaned by repeated cycles of argon ion sputtering and annealing. The surface was exposed to H₂O or D₂O gases via a tube doser below 20 K. We conducted the experiments at very

low coverages, where water molecules exist mainly as isolated monomers and dimers on the surface.

A water dimer is characterized by its bi-stable fluctuating image due to the interchange motion of the hydrogen-bond donor and acceptor molecules. The STM image of the dimer shows dramatic change upon substitution with heavy water. The interchange motion of (D₂O)₂ is much slower than that of (H₂O)₂. The interchange rate was determined to be $(6.0 \pm 0.6) \times 10^{-1} \text{ s}^{-1}$ for (H₂O)₂ and $1.0 \pm 0.1 \text{ s}^{-1}$ for (D₂O)₂ by monitoring the interchange events in real time. The large isotope effect (~60) suggests that the rate-limiting process involves quantum tunneling. In addition, DTF calculation revealed that the barrier of the interchange on Cu(110) is 0.24 eV. This cannot be overcome via mere thermal process at 6 K, which corroborates that the interchange proceeds through tunneling.

Furthermore, the interchange rate is enhanced upon excitation of the intermolecular mode that correlates with the reaction coordinate. While the interchange motion is intrinsic at low bias voltage, as indicated by negligible tip effect, it becomes tip assisted at voltages above 40 mV. The threshold voltage is determined to be 45 ± 1 (41 ± 1) mV for H₂O (D₂O) dimers. The barrier for the interchange (0.24 eV), however, much larger than the energy transferred from a tunneling electron (45 mV). Consequently, we propose that the interchange tunneling is assisted by vibrational assisted tunneling process.

[1] R. S. Fellers, C. Leforestier, L. B. Braly, M. G. Brown, and R. J. Saykally, *Science* 284, 945 (1999).

[2] T. Kumagai *et al. Phys. Rev. Lett.* 100, 166101 (2008).

2:40pm **SS2-WeA3 Single Molecule Assembly, Chirality and Catalysis.** C.E. Sykes, Tufts University **INVITED**

Self-assembled monolayers (SAMs) offer many useful applications in the form of parallel nanostructure fabrication, lubricants for MEMS, corrosion protection and sensing. Thioethers are more resilient to oxidation than thiols and offer the potential for control over nanoscale assembly in two dimensions parallel to the surface. Low-temperature scanning tunneling microscopy (LT-STM) data demonstrates that thioethers form large, very well ordered domains with little or no defects that cover areas >1,000nm². In contrast to alkane thiol assembly on the same surface, thioethers do not lift the Au {111} herringbone reconstruction. This feature facilitates defect-free thioether assembly which is not disrupted by etch-pit formation that alkane thiol SAMs suffer from. These data suggest the potential use of thioethers for a variety of self-assembly applications that require very perfect assembly and control over molecular spacing parallel to the surface.

Thioethers also constitute a simple, robust system with which molecular rotation can be actuated thermally, mechanically and electrically. By monitoring the rate of rotation as a function of tunneling electron energy (action spectroscopy) we have demonstrated that the rotors can be driven electrically via a mechanism that involves excitation of a C-H stretch. Forming ordered arrays of molecular rotors may provide entirely new approaches to signal processing, sensing, and energy modulation. For this application, an array of dibutyl sulfide rotors has been formed on a Ag/Cu{111} surface alloy. Molecular rotors can also act as standards by which scanning probe chirality can be measured and assigned. Such atomic-scale geometric data about the STM tip allows unambiguous chirality assignment on individual, isolated, molecule basis for the first time.

Palladium and its alloys play a central role in a wide variety of industrially important applications such as hydrogen reactions, separations, storage devices, and fuel cell components. The exact mechanisms by which many of these processes operate have yet to be discovered. LT-STM has been used to investigate the atomic-scale structure of Pd/Au and Pd/Cu bimetallics created by depositing Pd on both Au(111) and Cu(111) at a variety of surface temperatures. We demonstrate that individual Pd atoms in an inert Cu matrix are active for the dissociation of hydrogen and subsequent spillover onto Cu sites. Our results indicated that H spillover was facile on Pd/Cu at 400 K but that no H was found under the same H₂ flux on a Pd/Au sample with identical atomic composition and geometry.

4:00pm **SS2-WeA7 Molecular Motion in Confinement.** Z. Cheng, M. Luo, D. Sun, L. Bartels, University of California at Riverside

CO diffusion within a honeycomb network of anthraquinone molecules on a Cu(111) will be presented. The motion of the molecules is strongly affected by the confinement provided by the network. We observe the formation of a shell structure within pores, diffusion rates that strongly depend on the coverage and imperfections of the coverage (e.g. dislocation lines) that appear thermodynamically stable.

* Morton S. Traum Award Finalist

4:20pm **SS2-WeA8 Spatial Images of Different Vibronic Peaks at Single Molecule Level**, *Q. Huan*, University of California, Irvine and Chinese Academy of Sciences, *H.J. Gao*, Chinese Academy of Sciences, *W. Ho*, University of California, Irvine

Spatial distributions of different vibronic peaks on single naphthalocyanine molecules adsorbed on an ultrathin aluminum oxide film are imaged by a scanning tunneling microscope in real space at low temperature. The spatial variations of electron-vibronic coupling in these images reveal the interplay between the molecular conformation, the vibrational modes and the molecular orbital structure, which are in accordance with spectra recorded at different locations over the molecule.

This work shows that vibronic imaging can provide rich information of electron-vibrational coupling at the single molecule level.

4:40pm **SS2-WeA9 Stepwise Control and Spectroscopic Manifestation of the Target-Selective Single Bond Dissociation and Formation**, *Y.J. Jiang*, *W. Ho*, University of California, Irvine

We demonstrated here, adopting a thiol-based π -conjugated molecule (1,4-bis[4'-(acetylthio)styryl]benzene), the evolution of the molecular electronic structure with the stepwise abstraction of different functional groups and the attachment of single gold atoms to sulfur anchoring atoms by scanning tunneling microscope (STM). The electronic resonances of the resultants were measured by spatially resolved electronic spectroscopy at each reaction step. It was revealed that the target-selective bond dissociations were initiated by electron populations of the spatially localized and energetically separated electronic resonances. Combining the well-controlled single bond scission with the lateral manipulation by STM tip, the details of Au-S bond formation and the influence of Au-S interaction on the electronic structure of the molecular junction were investigated in the well-defined contact geometry.

5:00pm **SS2-WeA10 Surface Dynamics of Molecules in Single Internal (Vibrational and Rotational) States**, *V.L. Campbell*, *N. Chen*, *A.L. Utz*, Tufts University

Beam-surface scattering studies of molecules prepared in a single internal quantum state provide a high level of control over the energetics and internal motion of the gas-phase reagent. Varying the identity of the laser-excited state permits a systematic survey of how vibrational excitation in the gas-phase reagent (bending or stretching excitation) impacts reactivity and reveals that both vibrational mode-selective and bond-selective chemistry is possible in a gas-surface reaction. Recently, we have begun to exploit the energetic control this approach offers to probe the dynamics of other energetic degrees of freedom. For example, state resolved reactivity measurements (S_0 vs. E_{trans}) of CH_4 dissociation on Ni(111) show that the shape of the sticking curve changes as a function of surface temperature. This change likely results from the modulation of the effective barrier to reaction along the translational energy coordinate as a function of surface atom position. Our experimental results are consistent with recent theoretical studies that point to an important role for surface atom motion in promoting dissociative chemisorption on Ni and Pt surfaces. The presentation will focus on our use of state-selected reagents to probe dynamics associated with other energetic degrees of freedom, such as surface atom motion. It will also describe advances in our experimental methods for acquiring these state-resolved data. These advances are transforming our ability to perform state-resolved measurements and will enable our extension of these methods to a much wider array of chemical systems.

5:20pm **SS2-WeA11 3-Dimensional Velocity Map Imaging from Surfaces: A New Technique for the Study of Photodesorption Dynamics**, *S.P. Koehler*, *Y. Ji*, University of California, Santa Barbara, *D.J. Auerbach*, GRT Inc., *A.M. Wodtke*, University of California, Santa Barbara

The ion imaging technique and the improved velocity map imaging (VMI) technique [1] have been successfully applied to many gas-phase photo-dissociation and crossed-beam experiments over the last 20 years [2]. The VMI technique maps two dimensional product velocity distributions to an image on a position sensitive detector and thus allows the measurement of product flux as a function of velocity for all velocities simultaneously.

Experiments on photo-desorption from surfaces have so far not used this elegant technique. Such experiments have often relied on time-of-flight (TOF) techniques to gain dynamical information about the process under investigation [3].

Here we show how Time-of-Flight (TOF) measurements can be coupled to the VMI technique to yield 3-dimensional velocity distributions for desorption products of surface photochemistry. In one example, we applied this Three-Dimensional Surface Velocity Map Imaging (TDS-VMI) method to measure 193 nm photo-desorption of Br atoms from a KBr surface. Although this system has been studied in the past, the TDS-VMI technique reveals new features of the desorption dynamics. The velocity distributions

indicate that at least two non-thermal mechanisms contribute to the photo-desorption dynamics. The TDS-VMI method also allows us to measure the yield of $\text{Br}(^2P_{3/2})$ and $\text{Br}(^2P_{1/2})$ over the full range of velocities that contribute to the photo-desorption process. The branching ratio $\text{Br}(^2P_{3/2})/\text{Br}(^2P_{1/2})$ is 24/1, a value that is quite different from that obtained previously.

Other examples will be discussed at the conference.

5:40pm **SS2-WeA12 Activated Quantum Diffusion of Hydrogen on Platinum(111)**, *A.P. Jardine*, *E. Lee*, *G. Alexandrowicz*, *H.J. Hedgeland*, *W. Allison*, *J. Ellis*, University of Cambridge, UK

Hydrogen atoms are one of the few surface species that are of sufficiently low mass for quantum processes to dominate surface transport. Here, we present the first quasi-elastic helium atomscattering (QHAS) measurements that demonstrate clear quantum effects in adsorbate diffusion. We use helium-3 spin-echo to make dynamic equilibrium measurements of the motion of H and D atoms on a Pt(111) surface, enabling lower temperatures to be studied than were possible with QHAS[1]. Our data shows a broken Arrhenius dependence, indicating two transport regimes; high temperatures (>120 K) and low temperatures (<110 K). Otherwise, the data shows good agreement with a single jump model.

Our results offer a comprehensive dataset that is a severe test of theory. We compare the experimental data to existing protonic band structure calculations[2]. For H, it is possible to relate the measured activation energies to transitions to specific excited states of H, suggesting the diffusion of H on Pt(111) proceeds by activated quantum tunnelling. For D, the correspondence is less clear. We see a large change in pre-exponential factors with temperature, but not isotope, which we relate to energy exchange between adatoms and the surface. We compare the apparent rates of hopping with the expected tunnelling and energy transfer rates, in order to identify the rate limiting processes.

Recent work suggests that surface steps determine the macroscopic behaviour. However, our measurements are sensitive to the local, microscopic behaviour and give an alternative picture of the quantum motion[3].

[1] A. P. Graham, A. Menzel and J. P. Toennies, *J. Chem. Phys.* 111, 1676 (1999).

[2] S. C. Badescu, P. Salo, T. Ala-Nissila, S. C. Ying, K. Jacobi, Y. Wang, K. Bedurftig and G.Ertl, *Phys. Rev. Lett.* 88, 136101 (2002).

[3] C. Z. Zheng, C. K. Yeung, M. M. T. Loy, and Xudong Xiao. *Phys. Rev. Lett.* 97, 166101 (2006).

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