Surface Science
Room: C-112 - Session SS-WeM

New Opportunities and Technique Innovations
Moderator: A.R. Laracuente, Naval Research Laboratory

8:20am **SS-WeM1 Surface Vibrational Spectroscopy Beyond the Harmonic Approximation: Experiments and ab initio Calculations of Ethoxy Adsorbed on Cu(100)**, ***M.P. Andersson***, *P. Uvdal*, Lund University, Sweden

We compare high sensitivity experimental reflection-absorption IR spectra of ethoxy adsorbed on Cu(100) with ab initio calculations. The high sensitivity allows for detection of binary combinations of CH bend modes, i.e. overtones and combination bands. As their presence cannot be explained using a strictly harmonic approximation, we include anharmonic effects in the ab initio treatment as well. Calculations at the harmonic level are performed for an ethoxy-Cu17 cluster with a hybrid DFT method. Anharmonic effects are computationally more demanding and are therefore calculated for the free ethanol molecule using the same method and basis set as for the cluster. The anharmonic effects are then added through a standard expression involving third and fourth derivatives of the energy. The method allows for inclusion of both intramode anharmonicity and anharmonic resonance effects such as Fermi resonances due to accidental degeneracy. The experimental spectrum is reproduced in detail, including CH bend overtones and combination bands in resonance with CH stretch fundamentals. The mean absolute deviation is only 10 cm-1 and all intensities are also very well reproduced.

8:40am **SS-WeM2 Development of a Time-of-Flight HREELS Using Pseudorandom Modulation**, ***R.H. Jackson***, *Z. Yang, L.J. LeGore, P. Kleban, B.G. Frederick*, University of Maine

We have constructed a prototype high resolution Time-of-Flight HREELS utilizing pseudorandom modulation. The instrument is comprised of an LK-3000 HREELS, a custom designed TOF analyzer with a double mu-metal shielded 1.5m flight tube, a Bradbury-Neilsen Gate modulator, a microchannel plate detector, and a Fast Com Tek time to digital converter with 250 ps time bins. The electron optics have been shown to pass a beam of electrons to the detector with energies as low as 0.5eV over a 1m flight length. The TOF spectra are recovered using the Lucy maximum likelihood deconvolution algorithm. Initial measurements show that the method can recover well resolved <4meV peaks at 6eV flight energies to within the capability of the current data acquisition electronics. We will present the methodology for using and calibrating the instrument and show loss spectra of PTFE films comparing the TOF and conventional spectra.

9:00am **SS-WeM3 The STM as Operative Tool: Physics and Chemistry with Single Atoms and Molecules**, ***K.H. Rieder***, Free University Berlin, Germany **INVITED**

Recent progress in using the scanning tunneling microscope (STM) for manipulation of individual atoms and molecules is reviewed. Topics include - build-up of artificial nanostructures by lateral manipulation (pulling, pushing, sliding) - determination of physical properties like electron phase relaxation lengths in artificial structures - manipulation and contacting of complex molecules as well as manipulation into parts of molecules with consequences to molecular electronics - induction of all steps of chemical reactions with tips funcionalized by vertical manipulation - investigation of electronic and vibrational influences upon electron induced formation of ice clusters - experiences with attempts to transfer manipulation techniques from metal surfaces to thin insulating films. * In collaboration with: Gerhard Meyer (IBM ZRL), Francesca Moresco, Karina Morgenstern, Ludwig Bartels (UC Riverside), Kai-Felix Braun, Stefan Falsch (PDI-Berlin), Saw-Wai Hla (Ohio State Univ.), Reinhold Koch (PDI-Berlin), Jascha Repp (IBM ZRL), Jens Schulz (PDI-Berlin), Sven Zaphel (Createc)

9:40am **SS-WeM5 Microscopic Nature of the Interaction of Water with Noble Metal Surface**, ***H. Fukidome***, *Y. Kim,* RIKEN, Japan, *Y. Sainoo,* University of Tsukuba, Japan, *T. Komeda,* RIKEN, Japan, *H. Shigekawa,* University of Tsukuba, Japan, *M. Kawai*, RIKEN, Japn

Interaction of water on solid surfaces has been one of the central issues in science.It has been, however, hard to microscopically investigate the interaction of water with solid surfaces by traditional macroscopic spectrscopies, such as infrared spectroscopy and electron energy-loss spectroscopy. One of the reasons for this is that water can form various types of cluster owing to its hydrogen-bonding. A STM-IETS, which can do a spectroscopy at a sinlge-molecular level,[1] was used in our work in order to microscopically study the interaction of water with Pd(110) surface. In our STM-IETS spectra of water monomer, a huge and asymmetrical feature appeared at 57 meV. This can be assigned to the frustrated translational mode of water perpendicular to the surface (Tz).[2] On the contrary, no feature was absent at 57 meV in a spectra of water tetramer. The above-mentioned asymmetrical lineshape of the Tz mode of water monomer arises from the interference between elastic and inelastic tunneling processes. More interestingly, the lineshape of the Tz mode drastically changed within the molecule. This drastic change is caused by the mixing of two molecular orbitals that are responsible for the tunneling processes associated with Tz mode. A comparison between our STM-IETS results and a detailed theory now under construction would tell the microscopic picture of the interaction of water molecules with metal surfaces that has ever remained to be seen.

[1] B.C. Stipe, M.A. Rezaei, and W. Ho, Science 280 (1998) 1732.
[2] R. Brosseau, T.H. Ellis, and M. Morin, J.Vac.Sci.Technol. A8 (1990) 2454.

10:00am **SS-WeM6 First Principles Simulation for NC-AFM Images of Si(111) Ö3xÖ3-Ag Surface**, *N. Sasaki,* University of Tokyo and Japan Science and Technology Corp. (JST), Japan, *S. Watanabe,* ***M. Tsukada***, University of Tokyo, Japan

Quantitative, or sometimes even qualitative interpretation of non-contact atomic force microscopy NC-AFM images is extremely difficult, which contracts with the case of STM (scanning tunneling microscopy). Therefore theoretical simulations of NC-AFM images based on the first-principles density functional theory play very important role for the analyses of the experimental date. Effects of the tip structure and atom kind dependence can be also clarified, by the theoretical simulation. There have been some extrordinary features have been experimentally reported for the Si(111) √3x√3 surface(refferd to √3-Ag hereafter), which await theoretical explanation. Recently Scanning Tunneling Microscopy (STM) experiment of √3-Ag surface have been reproduced well based on the assumption of fluctuated Ag atoms among different energetically stable phases of Inequivalent-Triangle (IET) structures[1] without the tip effects using Monte Carlo simulation.[2] However NC-AFM experiments of the √3-Ag surface at room temperature[3] have not been fully understood yet. Important point here is that, in the case of NC-AFM, the tip effects are much stronger than in the case of STM, which give remarkable influences on the surface dynamics.Therefore in this work, NC-AFM images of √3-Ag surface at both room and lower temperatures have been reproduced by DFT calculations.[4,5] First we report that calculated images successfully reproduce experimental ones for both room temperature[5] and lower one. For the room temperature image, thermal fluctuation is described by the weighted average of the two IET phases with the Boltzmann factor counting the difference of the interaction energies. Energetically stable IET structure appears in the lower temperature image. Thus it is clarified that, as far as only the room temperature NC-AFM experiment is observed, we cannot obtain information of truly stable IET structure of √3-Ag surface.Next we show a remarkable tip-height dependence of the lower temperature NC-AFM images. In this case the Hydrogen-terminated Si tip is used. As the tip approaches the surface the NC-AFM image pattern changes from that of IET phase to HCT phase, and another IET phase. We explain this transition from the standpoint of the atom relaxation of tip-surface system. Thus our calculated results mean that Scanning Probe Microscopy (SPM) has an ability of not only directly observing dynamic feature of the surface but also mechanically controling the surface structures.

[1] H. Aizawa, M. Tsukada, N. Sato, and S. Hasegawa, Surf. Sci. 429, L5c09 (1999).
[2] Y. Nakamura, Y. Kondo, J. Nakamura, and S. Watanabe, Surf. Sci. 493 206 (2001).
[3] Y. Sugawara et al., Surf. Interface Anal, 27, 456 (1999).
[4] N. Sasaki, S. Watanabe, H. Aizawa, M. Tsukada, Surf. Sci. 493, 188 (2001).
[5] N. Sasaki, S. Watanabe, M. Tsukada, Phys. Rev. Lett. 88, 046106 (2002).

10:20am **SS-WeM7 Single Molecular Motion and Reaction Induced by STM Inelastic Tunneling**, *Y. Sainoo,* RIKEN and Tsukuba University, Japan, *Y. Kim, T. Komeda,* ***M. Kawai***, RIKEN, Japan

Inelastically tunneled electrons using STM device enable vibration excitation of individual molecules applicable to vibration spectroscopy, mode selective reaction and so on. Here we present that the selective excitation is ruled reflecting the symmetry of adsorbed molecules and that the vibrationally excited molecules may react along the reaction coordinate through their multiple excitation state. Examples for selective excitation are given for trans-2-butene on Pd(110) surface where methyl groups are lifted towards vacuum and butadiene with flat-laying geometry. The C-H stretching vibration is clearly observed for trans-2-butene and not for butadiene. Symmetry of the adsorbed states for both adsorbates is determined by XAS and HREELS. Motions of isolated cis-2-butene molecule on the Pd(110) surface at 4.7 K between four equivalent positions were induced and monitored with tunneling electrons of scanning tunneling microscope (STM). These motions were consisted with two different flip-flop motions, and clear threshold energy indicated the existence of different potential barriers for the corresponding motions. The strong dependences of these motions rate on the tunneling current support multiple vibrational excitation mechanism via inelastic tunneling process.

10:40am **SS-WeM8 Dry De-intercalation in Layered Compounds upon Controlled Surface Charging in XPS**, *Y. Feldman, A. Zak, R. Tenne,* ***H. Cohen***, Weizmann Institute of Science, Israel

2H platelets and inorganic fullerene-like (IF) MS_2 (M=W,Mo) powders, intercalated with alkaline (A=K,Na) atoms,[1] are studied using controlled surface charging (CSC) in XPS.[2] The degree of intercalation, expressed in terms of A/M concentration ratios, is found to tightly correlate with the presence of 'open' (hk0) edges, typically absent from the closed IF nanoparticles. Under strong electric fields, applied by an electron flood gun, diffusion of the intercalants towards the surface is observed. This out-diffusion process is negligible with low flood gun voltages, indicating that a critical field is needed for this type of dry de-intercalation. Diffusion rates out of 2H matrixes are generally higher than in corresponding IF samples, while those of K are far better than Na. These observations, closely related with the initial intercalation efficiency, provide helpful information about the actual intercalation states and their diffusion mechanisms.

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[2] I. Doron-Mor, A. Hatzor, A. Vaskevich, T. van der Boom-Moav, A. Shanzer, I. Rubinstein and H. Cohen, Nature 406, 382 (2000).

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