Tuesday Morning, October 3, 2000

Surface Science
Room 210 - Session SS3+MC-TuM

Technique Innovations: Experiment, Theory and Simulation

Moderator: S.B. Sinnott, The University of Kentucky

8:20am **SS3+MC-TuM1 Twenty-First Century Modeling: Multiscale Coupling and its Impact on Surface and Interface Science***, **E.A. Carter**,* University of California, Los Angeles **INVITED**

Multiscale modeling is all the rage among computational material scientists in this new century. This refers to a type of simulation which considers phenomena whose length and/or time scales span several - possibly many - orders of magnitude. Examples of such phenomena include, e.g., time scale disparities in surface diffusion and thin film growth, length scale disparities in corrosion-induced cracking of solid materials, etc. In the first example, surface diffusion is "fast" while the flux of material is "slow". In the second example, corrosion involves chemical reactions on the atomic scale while cracking takes place on the meso-to-macroscale. Future materials modeling will account for the complexities across scales. An overview will be given of new techniques being developed that: (i) provide a first principles quantum mechanical description of thousands of atoms (via a linear scaling kinetic energy density functional - KEDF - theory); (ii) couple atomic level interactions, described by KEDF molecular dynamics simulations, to quasi-continuum simulationsof behavior on the micron scale; and (iii) connect first principles quantum mechanics calculations to cohesive zone continuum mechanics simulations of crack propagation in solids. The impact of such coupled simulations on understanding how surface and interface phenomena affect materials behavior on scales beyond the atomic will be emphasized.

9:00am **SS3+MC-TuM3 The KMLYP Density Functional Approximation: A New Method for Accurate Prediction of Activation Barriers and Enthalpies of Reaction***, J.K. Kang,* ***C.B. Musgrave*,** Stanford University

We develop the KMLYP hybrid DFT method which is shown to predict activation energies and enthalpies of reaction with smaller errors than B3LYP, G2, QCISD(T), CCSD(T), and CBS-APNO. The accuracy of the method is demonstrated on over 100 reactions. The KMLY P exchange functional is a hybrid functional that combines Hartree-Fock exact exchange with Slater exchange. The correlation functional is a hybrid functional combining Lee-Yang-Parr (LYP) correlation and Vosko-Wilk-Nusair (VWN) correlation. For reactions with reliable experimental data, the RMS deviation of the activation energies are 0.64 kcal/mol, 1.59 kcal/mol, 3.20 kcal/mol, and 3.10 kcal/mol for the KMLYP, CBS-APNO, G2, and B3LYP methods, respectively. The RMS deviations from experiment of the entha lpy of reaction are 1.57 kcal/mol, 2.24 kcal/mol, and 2.87 kcal/mol for the KMLYP, G2 and B3LYP methods, respectively. The KMLYP maximum absolute deviation of the activation barriers is 1.2 kcal/mol while the KMLYP maximum absolute deviation of the enthalpy of reactions is 3.8 kcal/mol. Furthermore, KMLYP is significantly more efficient than the G2, QCISD(T), CCSD(T), and CBS-APNO methods and is practical for the simulation of surface reactions using relatively large clusters.

9:20am **SS3+MC-TuM4 Probing Chemical Interactions at the Single Bond Level***, **M.K. Weldon**,* Bell Laboratories, Lucent Technologies*; J.D. Batteas,* City University of New York, College of Staten Island*; K. Raghavachari,* Bell Laboratories, Lucent Technologies

The measurement of chemical bond strengths is a fundamental goal of much of chemistry; indeed the making and breaking of bonds between atoms is the essence of chemical science. Despite this, the direct measurement of bond strengths has remained an elusive goal due primarily to the inherent difficulty in localizing the requisite excitation along a single bond coordinate. Here we demonstrate a methodology for measuring the strength of individual chemical bonds at solid surfaces. We have used atomic force microscopy (AFM) to probe the pH-dependent changes in the surface chemistry of silica in the single bond limit. We observe quantized adhesion forces that, when referenced to the results of ab initio quantum chemical cluster calculations, can be unambiguously assigned to single neutral hydrogen bonds (OH..OH), single ionic hydrogen bonds (OH@super -@..OH) and single covalent bonds (Si-O-Si) between the tip and surface. We have subsequently extended this work to measure the interaction (bond) energetics in a number of aqueous and organic solvent systems. Remarkably, we find that we able to observe individual H@sub 2@O..H@sub 2@O hydrogen bonds under the appropriate conditions, as well as the attendant isotopic shift and bond weakening upon raising the temperature, again demonstrating the potential of this approach for exploring the nature of chemical bonds in solution. In summary, this breakthrough in chemical analysis is predicted to be generalizable to all solution reactions for which the constituent reagents can be chemically functionalized onto a solid surface. To this end, we are currently investigating the interaction energetics in a variety of reactive organic systems.

9:40am **SS3+MC-TuM5 Surface Vibrational Spectroscopy Beyond the Harmonic Approximation, Experiments and Calculations***, **P. Uvdal**, M.P. Andersson, R. Asmundsson,* Lund University, Sweden*; A.D. MacKerell, Jr.,* University of Maryland

Vibrational analysis of surface adsorbates involves in general the assignment of fundamental normal modes. Based on such assignment conclusions about chemical identity and geometry can be drawn. It is however well known from fundamental textbooks on molecular vibrations that if one goes beyond the harmonic approximation of the intramolecular bond potential overtone and combination modes are allowed. Binary modes, i.e. excitation of one vibration with two quanta or excitation of two vibrations with one quanta, will be the most intense even though higher excitations are allowed. The presence or absence of binary modes will contain information about bond anharmonicity and coupling between different modes. The latter may reveal surface induced changes of activation barriers of importance for the understanding of e.g. heterogeneous catalysis. The former reveal dynamical properties of the system as the extent of coupling governs the dissipation and randomization, within the molecule, of the energy initially localized in a single bond excitation. Using methoxy and ethoxy adsorbed on Cu(100) and W(110) surfaces as model systems we will demonstrate binary intramolecular modes in the presence and absence of Fermi resonance coupling. We will also show a combination mode consisting of the C-O stretch and the hindered motion of methoxy with respect to the surface.

10:00am **SS3+MC-TuM6 Time Resolved Fourier Transform Infrared Spectroscopy***, **M. Kovar**, P.R. Norton,* University of Western Ontario, Canada

We have developed a data acquisition system based on digital signal processing for a broadband time-resolved Fourier Transform Infrared Spectrometer. In FTIRS, broadband infrared radiation is modulated by means of a Michelson interferometer. The position of the moving mirror is tracked by the fringe pattern of a reference He/Ne laser, whose beam follows the same optical path as the infrared radiation. Pulses used for time resolution as fast as 500 ns are modulated on a reference He/Ne laser signal. We have chosen a slower mirror speed which permits observation of an external perturbation of a system under investigation which often limits the mirror speed. Different external perturbations can be used, such as thermal, mechanical, photochemical or those caused by external potential. We discuss characteristics of time resolved FTIRS and its performance. The system will permit grazing incidence IR reflection-absorption measurements of surface and thin film processes with sub-microsecond time resolution.

10:20am **SS3+MC-TuM7 Momentum Space Line Narrowing by Angle Resolved Auger-photoelectron Coincidence Spectroscopy***, A. Danese,* ***R.A. Bartynski*,** Rutgers University*; R. Gotter,* Lab. Nazionale TASC-INFM, Trieste, Italy*; S. Iacobucci,* CNR-IMAI Montelibretti, Italy*; G. Stefani,* U. di Roma III, Italy

We have measured the Ag N@sub 23@VV Auger electron diffraction pattern from the Ag(100) surface in coincidence with Ag 4p photoelectrons under high energy and angular resolution conditions. Measurements were performed using the ALOISA beamline at the ELETTRA synchrotron in Trieste. It is well known that the Auger and photoemission spectra associated with the shallow 4p (3p) core levels of the late 4d (3d) transition metals are unusually broad in energy owing to the rapid decay of the core hole. Furthermore, it has been shown for the Cu 3p and Ag 4p levels that this energy broadening can be eliminated in Auger-photoelectron coincidence (APEC) energy distribution curves. However, this lifetime broadening is expected to generate a concomitant momentum broadening and the resultant Auger diffraction pattern has only a very weak intensity modulation of ~15%. By performing an APEC measurement with high energy and angular resolution, this momentum broadening should be eliminated. In our APEC angular distribution curves, intensity modulations are enhanced to ~50%, consistent with a significant reduction of the momentum uncertainty of the outgoing Auger electrons. These results provide direct evidence that the photoexcitation/Auger decay of these levels is a coherent process. The implications of these results in the context of Auger electron diffraction will be discussed.@footnote 1@ @FootnoteText@ @footnote 1@ Supported by NSF grant NSF-DMR9801681 and NATO grant CRG97-0175.

10:40am **SS3+MC-TuM8 A Microarray Technique for Measuring Adsorption/Desorption Kinetics*, M.C. Wheeler,*** *R.E. Cavicchi, G.E. Poirier, S. Semancik,* National Institute of Standards and Technology

We have developed a novel method for characterizing the kinetics and thermodynamics of adsorption and desorption that uses a 340-element array of micromachined Si hotplates as the sample platform. The method takes advantage of the microhotplates' rapid heating characteristics (10@super 6@ °C/s), intermediate between traditional temperature programmed desorption methods and pulsed laser desorption. The method is isobaric, particularly useful for studying many systems where the desorption rate is significant at room temperature, and readily automated to efficiently produce large data sets for adsorption systems. Under constant gas exposure, all of the array elements are simultaneously subjected to square temperature pulses as short as 5 ms. An example sequence is a high-T cleaning pulse (as high as 800 °C), a low-T adsorption pulse, an intermediate-T desorption pulse, and a final high-T cleaning pulse. Variation of the pulse amplitude and duration allows determination of the adsorption and desorption rate constants and energies. Signal-to-noise is enhanced by using a large array of microhotplate devices and averaging of repeated pulse sequences. The pressure range is extended to over 10@super -5@ Torr using a differentially pumped mass spectrometer system (even higher effective pressures can be achieved with a directed doser). We illustrate the technique by mapping adsorption isotherms and extracting parameters for methanol on CVD-deposited SnO@sub 2@ polycrystalline films, such as are used in gas sensing; however, wide ranges of materials and adsorbates can be investigated with this technique. In addition to emphasizing the convenience, flexibility, simplicity, and efficiency of this automated technique, we will also discuss challenges that we have had to address - the most significant relating to temperature calibration and uniformity.

11:00am **SS3+MC-TuM9 Scanning Probe Energy Loss Spectroscopy: Spectroscopic Analysis of Reflected Electrons in Field Emission STM*, B.J. Eves,*** University of Birmingham, UK*; F. Festy, K. Svensson,* University of Birmingham, UK, U.K.*; R.E. Palmer,* University of Birmingham, UK

Spectroscopic (i.e. chemical) analysis is a key frontier in scanning probe microscopy. We have employed a scanning tunnelling microscope (STM) operating in field emission mode to act as a nanometre scale electron source while the resulting backscattered electrons have been detected with a hemispherical energy analyser. Angular measurements show that the flux of reflected electrons peaks parallel to the surface, consistent with simulations which include the long range field generated by the tip bias voltage. The measured energy loss spectra contain information on the surface and bulk plasmons, and other surface excitations. The Si (111)-7x7 surface was found to show losses at 5, 7.5, 11, 15, and 18 eV. These inelastic losses correspond to an interband transition (5 eV), two surface states (7.5 and 15 eV), and the surface and bulk plasmons (11 and 18 eV, respectively). Spectra have also been measured for a number of different exit angles. With improvements it is believed that the scanning probe energy loss spectrometer (SPELS) can be built to perform electron energy loss spectroscopy with spatial resolution on the scale of 5-50 nm.

11:20am **SS3+MC-TuM10 Application of a Direct Method in Surface X-ray Crystallography*, P.F. Lyman,*** *R. Harder, D.K. Saldin,* University of Wisconsin, Milwaukee*; C.-Y. Kim, K.W. Evans-Lutterodt,* Lucent Technologies

The electron density of the near-surface region of a crystal could be recovered from x-ray scattering data if the phases of the scattered radiation were known. In the case of surface scattering, the diffracted intensities arise from the square of a linear combination of bulk and surface amplitudes. Since the phases and amplitudes of the bulk component can be calculated accurately, it is possible to use the bulk scattering as a reference wave, and to thereby estimate the phases of the surface component, in analogy with holography. We have developed an algorithm to estimate the most likely set of surface phases, and to thereby recover the electron density of the near-surface region. We present preliminary applications of this method to (2x1)-reconstructed Ge(001) surfaces. It has been shown that the (001) face of Ge or Si can be passivated by 1 ML of a group V element. Although there is general acceptance of the existence of symmetric group V dimers for most adsorbate/substrate combinations, a controversial result of asymmetric Sb dimers for the Sb/Ge(001) system was concluded from an x-ray scattering study: Each Sb dimer was found to have shifted along the axis of the Sb-Sb bond.@footnote 1@ However, a number of first-principles calculations have found no evidence for the shift. We will use our direct reconstruction algorithm on experimental x-ray scattering data to address the possibility of shifted dimers in a model-independent way. @FootnoteText@ @footnote 1@ M. Lohmeier, H.A. van der Vegt, R.G. van Silfhout, E. Vlieg, J.M.C. Thornton, J.E. Macdonald and P.M.L.O. Scholte, Surf. Sci. V. 275, p.190 (1992).

11:40am **SS3+MC-TuM11 Line of Sight Techniques: Providing an Inventory of all Species Arriving at and Departing from a Surface*, R.G. Jones,*** University of Nottingham, UK, U.K.*; A.S.Y. Chan, M.P. Skegg,* University of Nottingham, UK

Line of sight techniques comprise those methods in which species emanating from a surface (atoms, molecules and radicals) undergo just a single pass through the ionisation volume of a mass spectrometer before being pumped. This is achieved by enclosing the mass spectrometer within a cryoshield fitted with appropriate apertures, such that line of sight is established only between a patch on the sample surface (ca 7 mm diameter) and the ionisation volume. All LOS techniques are inherently angle resolved, free from extraneous signals and have approximately equal detection probabilities for all species. Line of sight temperature programmed desorption (LOSTPD)@footnote1@ is a particularly reliable way of obtaining TPD data. By applying an over pressure of gas to the sample and monitoring the reflected flux, we get line of sight sticking probability (LOSSP) measurements@footnote 2@ giving S to an accuracy of 0.02; while monitoring of the reaction products at constant temperature gives line of sight product desorption (LOSPD) data. These techniques provide new, powerful and reliable ways of studying all aspects of surface kinetics, by allowing an inventory of all species arriving at and departing from a surface, for any combination of partial pressures, surface temperature, surface composition and surface structure. In this paper we illustrate these methods using the reactions of 1-bromo-2-chloroethane (BCE) and ioodotrifluoromethane with Cu(111). For BCE we show that it undergoes non-activated dissociative adsorption with a transition state 13 kJ/mol below zero (0 = molecule at infinity). For CF@sub3@I we observe emission of CF@sub3@ radicals and coupling reactions forming, among others, C@sub2@F@sub4@. @FootnoteText@ @footnote 1@ R.G. Jones and S. Turton, Surface Sci. 377-379 (1997) 719. @footnote 2@ R.G. Jones and C. J. Fisher, Surface Sci. 424 (1999) 127.

Author Index

Bold page numbers indicate presenter

— A —

Andersson, M.P.: SS3+MC-TuM5, 1

Asmundsson, R.: SS3+MC-TuM5, 1

— B —

Bartynski, R.A.: SS3+MC-TuM7, **1**

Batteas, J.D.: SS3+MC-TuM4, 1

— C —

Carter, E.A.: SS3+MC-TuM1, **1**

Cavicchi, R.E.: SS3+MC-TuM8, 2

Chan, A.S.Y.: SS3+MC-TuM11, 2

— D —

Danese, A.: SS3+MC-TuM7, 1

— E —

Evans-Lutterodt, K.W.: SS3+MC-TuM10, 2

Eves, B.J.: SS3+MC-TuM9, **2**

— F —

Festy, F.: SS3+MC-TuM9, 2

— G —

Gotter, R.: SS3+MC-TuM7, 1

— H —

Harder, R.: SS3+MC-TuM10, 2

— I —

Iacobucci, S.: SS3+MC-TuM7, 1

— J —

Jones, R.G.: SS3+MC-TuM11, **2**

— K —

Kang, J.K.: SS3+MC-TuM3, 1

Kim, C.-Y.: SS3+MC-TuM10, 2

Kovar, M.: SS3+MC-TuM6, **1**

— L —

Lyman, P.F.: SS3+MC-TuM10, **2**

— M —

MacKerell, Jr., A.D.: SS3+MC-TuM5, 1

Musgrave, C.B.: SS3+MC-TuM3, **1**

— N —

Norton, P.R.: SS3+MC-TuM6, 1

— P —

Palmer, R.E.: SS3+MC-TuM9, 2

Poirier, G.E.: SS3+MC-TuM8, 2

— R —

Raghavachari, K.: SS3+MC-TuM4, 1

— S —

Saldin, D.K.: SS3+MC-TuM10, 2

Semancik, S.: SS3+MC-TuM8, 2

Skegg, M.P.: SS3+MC-TuM11, 2

Stefani, G.: SS3+MC-TuM7, 1

Svensson, K.: SS3+MC-TuM9, 2

— U —

Uvdal, P.: SS3+MC-TuM5, **1**

— W —

Weldon, M.K.: SS3+MC-TuM4, **1**

Wheeler, M.C.: SS3+MC-TuM8, **2**