

Wednesday Morning, November 15, 2006

Surface Science

Room 2004 - Session SS2-WeM

Electronic and Vibrational Excitations and Dynamics

Moderator: M. Trenary, University of Illinois, Chicago

8:00am **SS2-WeM1 Theory of Electron-Hole Pair Excitation in Chemisorption**, *M.S. Miziański, D.M. Bird*, University of Bath, UK; *M. Persson, S. Holloway*, University of Liverpool, UK

It has long been recognised that the excitation of electron-hole pairs is an important mechanism for the transfer of energy to a surface in the adsorption of molecules on metal surfaces. Interest in electron-hole pair excitation has been revived recently with the observation of 'chemicurrents'¹ and exo-electron emission following vibrational de-excitation.² These phenomena are fundamentally non-adiabatic processes and require a theoretical description which goes beyond the Born-Oppenheimer approximation. To do this using ab-initio time-dependent DFT is computationally very expensive. Our approach is to gain an insight into the adsorbate-surface interaction by considering a simple model system. We analyse the non-adiabaticity by solving the time-dependent, mean-field Newns-Anderson model in the wide-band limit. In our previous work³ we have used this model to explore the non-adiabatic behaviour of the occupation of the adsorbate energy levels and the energy transfer between adsorbate and the metal surface. We present an extension of this work to an analytic solution for the time-evolving spectrum of excited electrons and holes. We will use this model to demonstrate the evolution of the excitation spectrum for a range of model systems. ¹B. Gergen et al., *Science* 294, 2521 (2001). ²J. D. White et al. *Nature* 433, 503 (2005). ³M. S. Miziański, D. M. Bird, M. Persson and S. Holloway, *J. Chem. Phys.* 122, 084710 (2005).

8:20am **SS2-WeM2 Adsorption-State-Dependent Subpicosecond Photoinduced Desorption Dynamics**, *P. Szymanski, A.L. Harris*, Brookhaven National Laboratory; *M.G. White*, Brookhaven National Laboratory and SUNY Stony Brook; *N. Camillone III*, Brookhaven National Laboratory, Suffolk

Femtosecond laser excitation has been used to initiate desorption of molecular oxygen from the (111) surface of Pd and study the adsorption-state-dependence of the substrate-adsorbate coupling. The relative populations of the two chemical states, peroxy (O_2^{sup-}) and superoxy (O_2^{sup-}), were varied by changing the total coverage. Two-pulse correlation measurements reveal that the O_2^{sup-} -substrate coupling times are dominated by a sub-500 fs response that is independent of O_2^{sup-} coverage. In contrast, the measurements show a systematic coverage dependence of the photodesorption yield and the nonlinearity of the fluence-dependence. Thus, though the photoinduced desorption from the two states is driven primarily by the same electron-mediated mechanism, the desorption efficiency from the superoxy state is greater than that from the peroxy state. These results are discussed in the context of the two-temperature model, treating the dependence of the desorption yield on absorbed laser fluence together with the dynamics in a global simulation to extract coupling strengths and understand the adsorption-state-dependence of the desorption efficiency.

8:40am **SS2-WeM3 High Resolution Photoemission as a Probe of the Collective Excitations in Condensed Matter Systems**, *P.D. Johnson*, Brookhaven National Laboratory

INVITED

Recent advances in photoemission are allowing detailed studies of the role of collective many-body excitations in the decay of a photohole. The collective excitations include phonons, charge density waves and magnetic or spin excitations. With these developments angle resolved photoemission with its momentum resolving capabilities has become a powerful probe of the transport properties in condensed matter systems. We review these advances and examine the application of photoemission to studies of both metallic systems and strongly-correlated materials. The latter exhibit a rich variety of phenomena including high T_c superconductivity. In particular, we examine the nature of the low-energy excitations and the role of dimensionality.

9:20am **SS2-WeM5 The Origin of Work function Changes Induced by Adsorbates on Metal Surfaces: A Theoretical Analysis**, *P.S. Bagus*, University of North Texas; *C. Wöll*, Ruhr-Universität Bochum, Germany

Adsorbates may induce large shifts in the work function, ϕ , of a metal surface. A traditional explanation of work function changes has been in terms of charge transfer, CT, between the substrate and the adsorbate with CT from the adsorbate to the substrate leading to a decrease in ϕ and to an increase in the interface dipole, as for alkali atom adsorbates.¹ For covalently bonded CO/Cu, the CT interpretation of $\Delta\phi > 0$ suggests a Cu-CO interaction dominated by σ donation.² However, weakly bound physisorbed adsorbates³ on metal surfaces also induce large $\Delta\phi$ and this cannot easily be explained by CT. For physisorbed species, the Pauli exclusion principle, which requires that an electronic wavefunction is anti-symmetric, has been shown⁴ to make a large contribution to the $\Delta\phi$. On Cu(111), we have studied the $\Delta\phi$ induced by several adsorbates, Xe, C_6H_{12} , C_6H_6 , CO, Cs, and I, representative of quite different types of bonding to the surface. The origins of the changes in the interface dipole are interpreted based on a decomposition into individual contributions from: (1) Pauli exclusion; (2) Polarization of the metal substrate; (3) Covalent bonding; and (4) Charge transfer. More than one contribution to $\Delta\phi$ may be large. The theoretical approach used is based on ab initio electronic structure theory applied to models of an adsorbate on a cluster of atoms representing the surface.⁴ We provide a unified understanding that makes it possible to correctly relate $\Delta\phi$ to the chemistry of the adsorbate-substrate bond. ¹J. P. Muscat and I. P. Batra, *Phys. Rev. B*, 34, 2889 (1986). ²D. Heskett et al., *Phys. Rev. B*, 32, 6222 (1985). ³P. S. Bagus, V. Staemmler, and C. Wöll, *Phys. Rev. Lett.*, 89, 096104 (2002). ⁴P. S. Bagus, K. Hermann, and C. Wöll, *J. Chem. Phys.* 123, 184109 (2005).

9:40am **SS2-WeM6 Rotational Disorder in Ordered Overlayer Phases**, *E.Z. Ciftlikli, I.G. Shuttleworth, A.V. Ermakov, J. Lallo, S. Rangan*, Rutgers, State University of New Jersey; *S.D. Senanayake*, Oak Ridge National Laboratory; *B.J. Hinch*, Rutgers, State University of New Jersey

CN containing moieties, such as C_2N_2 , $CN^{\sup-}$, CH_3CN and NCO species, are frequently observed as reactants, products and intermediates in many industrial heterogeneous catalytic processes. Despite their importance, there are relatively few published reports on the structure and dynamics of these species on metallic fcc close packed faces. It may be that electron and/or photon induced damage has hindered many such studies. Helium atom scattering (HAS), employing thermal energy atoms of $E < 100$ meV, is free of any detrimental/destructive effects. For example, angle resolved HAS measurements clearly show the existence of $c(10 \times 6)$ and $c(2 \times 2)$ ordered structures for $CN^{\sup-}/Cu(001)$ and $CH_3CN/Cu(001)$ surfaces, respectively. And yet energy resolved HAS measurements, which are designed to probe the low-energy vibrational modes of the bound moieties, do not indicate discrete low energy features associated with localized modes of the adsorbates. Broad multiphonon-like features dominate the TOF spectra, in both systems, and neither discrete frustrated translations, nor frustrated rotational modes are observed. Two contributions are apparent in the Near Edge X-ray Absorption Fine Structure (NEXAFS) spectra, suggesting that there are at least two CN species in the $CN^{\sup-}/Cu(001)$ system. One has horizontal alignment, the other shows no preferred spatial orientation. The NEXAFS measurements from the $CH_3CN/Cu(001)$ system suggest that there is only one type of adsorbate species, showing no preferred orientation. The lack of orientation observed in those ordered systems can imply that the surface moieties have a considerable degree of rotational freedom. DFT calculations have predicted low rotational barriers for adsorbed $CN^{\sup-}/fcc(001)$ systems. We discuss the helium scattering, as well as the NEXAFS spectra and analysis, in the light of this model for the dynamic adsorbate systems.

10:40am **SS2-WeM9 Mechanisms of Isomerization and Dehydrocyclization of n-Hexane on Pt(100) and Pt(111) Surfaces Studied with Sum Frequency Generation**, *K.M. Bratlie, G.A. Somorjai*, University of California, Berkeley
Using sum frequency generation (SFG) vibrational spectroscopy the adsorption geometries and surface reactions of various C_6 hydrocarbons (n-hexane, 2-methylpentane, 3-methylpentane, and 1-hexene) on a Pt(100) single-crystal surface was investigated. The adsorptions and reactions were carried out under pressures of 1.5 Torr of

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C@sub 6@ hydrocarbon in the presence and absence of hydrogen (15 Torr) and in the temperature range of 300 - 450K. At 300K and in the presence of excess hydrogen, n-hexane, 3-methylcyclopentane, 2-methylpentane, and 1-hexene adsorbed molecularly on Pt(100) in flat-lying geometries. Upon heating the surface temperature to 450K, both n-hexane and 3-methylpentane underwent dehydrogenation to form a surface species in a standing-up geometry: hexylidyne. 2-Methylpentane, however, was dehydrogenated to @pi@-allyl c-C@sub 6@H@sub 9@ at 375K. Further heating of the surface hydrogenated the adsorbed molecules to hexylidyne. Adsorbed 1-hexene remained unreacted as the temperature was increased. Subsequently cooling the surface temperature to 300K returned all the flat-lying hydrocarbons. The absence of excess hydrogen impeded surface reactions. Both 2-methylpentane and 1-hexene adsorbed intact and in flat-lying geometries. 3-Methylpentane and n-hexene dehydrogenate to form metallacyclohexane and flat-lying 1-hexene. All four adsorbates remained intact as the surface temperature was increased to 450K and, afterward, decreased to 300K. On the basis of these results, the mechanisms for catalytic isomerization and dehydrocyclization of n-hexane were elucidated.

11:00am **SS2-WeM10 Alane Formation on Al(111)**, *J.-F. Veyan, Y.J. Chabal*, Rutgers University

Complex metal hydrides, such as NaAlH@sub 4@, are candidates for hydrogen storage because they can reversibly release and recapture hydrogen under near ambient conditions. Surface processes in the hydrogen storage reaction in NaAlH@sub 4@, starting from a depleted phase consisting of NaH and metallic Al, and proceeding via cryolite Na@sub 3@AlH@sub 6@ to the hydrogen-rich NaAlH@sub 4@, are considered as the basis for understanding reversible hydrogen storage in the chosen prototype system. Since metallic Al, particularly when doped with other metals, appear key to H@sub 2@ dissociation, we have undertaken a comprehensive study of H interaction with Al(111) and Ti-doped Al(111) surfaces to better understand the atomic scale mechanisms underlying this reversible hydrogen storage behavior. Molecular hydrogen does not dissociate on pure, clean Al surfaces. However, below the desorption threshold of ~280K, atomic H interacts strongly with Al by extracting step and terrace atoms to form surface alane (AlH@sub 3@). Using IR spectroscopy, we have studied Al(111) after atomic H exposure and of Ti-doped Al(111) after H@sub 2@ exposure. The resulting spectra show the presence of alanes, characterized by terminal Al-H and bridging Al-H-Al termination. @footnote 1,2,3@ Preliminary experiments indicate that H@sub 2@ does dissociate on Ti-doped Al(111) surfaces, again forming alanes. The evolution of these oligomers as a function of substrate temperature will be discussed. @FootnoteText@ @footnote 1@ C. Liang, R. Davy, H.F. Schaefer III, Chem. Phys. Lett. 159 (1989) 393. @footnote 2@ B.J. Duke, C. Liang, H.F. Schaeffer III, J. Am. Chem. Soc. 113 (1991) 2884. @footnote 3@ M. Shen, C. Liang, H.F. Schaefer III, Chem. Phys. 171 (1993) 325.

11:20am **SS2-WeM11 Exploring Experimental Vibrational Spectra of Surface Adsorbates Using DFT Modeling**, *P. Uvdal*, Lund University, Sweden **INVITED**

Experimental vibrational spectra of small molecules adsorbed on single crystal metal surfaces are explored using DFT calculations. By combining high sensitive and high resolution (@>= 0.5 cm@super -1@) surface infrared spectroscopy and density functional calculations details in the spectra can be detected and analyzed. Strategies for analysis at both the harmonic and anharmonic levels are discussed. Overtone and combination modes in the absence and presence of Fermi resonances are also explored. Both cluster and extended structure calculations are utilized for investigation of the coordination site of the adsorbate on the surface. Methoxy and ethoxy adsorbed on Cu(100) and W(110) surfaces are used to show the interplay between experiments and calculations.

12:00pm **SS2-WeM13 Kinetics of NH Formation and Dissociation on Pt(111)**, *R.J. Meyer, K. Mudiyansele, M. Trenary*, University of Illinois at Chicago

The formation and dissociation of the NH species on the Pt(111) surface has been studied experimentally with reflection absorption infrared spectroscopy (RAIRS) and theoretically with density functional theory. NH is characterized by an intense and narrow peak at 3321 cm@super -1@, which allows the NH coverage to be accurately measured with RAIRS as a function of time. This permits the kinetics of an elementary surface reaction to be measured where neither the reactants nor products desorb from the surface. The experiment is performed by first preparing a well ordered p(2x2) N layer through oxydehydrogenation of NH@sub 3@, then

exposing to H@sub 2@ at low temperature. It is found that NH formation follows first-order kinetics with an activation energy of 0.23 eV, whereas the dissociation reaction follows second-order kinetics with an activation energy of 1.1 eV. Because NH is more stable on the surface than N and H, the dissociation kinetics are limited by the recombinative desorption of H₂, which accounts for the observed reaction order. The simplicity of this reaction provides an unusually favourable case for direct comparison between experimental measurements and theoretical calculations of the rate constant for a surface reaction. To gain further insight into experimental results, density-functional theory calculations were performed with the VASP program using a plane wave basis set and ultrasoft pseudopotentials. Rate constants were calculated based on the ratio of vibrational partition functions of the reactant and the transition state. Results indicate that the experimentally derived barrier from an Arrhenius analysis is much lower than that found in our DFT calculations using classical transition state theory. However, invoking a tunneling mechanism for NH formation readily explains this apparent discrepancy, and using an enhancement factor derived from semi-classical theory, we find very good agreement with experiment.

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