

Surface Science Division

Room 314/315 - Session SS3-TuA

Photon- and Electron-Induced Chemistry

Moderator: R.G. Tobin, Tufts University

2:00pm **SS3-TuA1 Photon Driven Chemistry of Adsorbates, J.M. White,** University of Texas, Austin **INVITED**

The photon driven chemistry of adsorbates on Ag(111) will be illustrated using results from sulfur dioxide, trifluoromethyl iodide and, in greater detail, methyl nitrite. The focus of the presentation will be a discussion of the angular and velocity distributions of nitric oxide moieties ejected from irradiated methyl nitrite. The dependence of these properties on photon energy (3 to 6 eV) and coverage (submonolayer to thick multilayer) is interpreted in terms of direct excitation of methyl nitrite with negligible contributions from substrate mediated processes. Comparisons with gas phase photochemistry of methyl nitrite will be made.

2:40pm **SS3-TuA3 Negative Ion Enhancement in Transport of Low Energy F@super -@ Ions Through Rare-Gas (Xe) Films, Q.B. Lu, T.E. Madey,** Rutgers, The State University of New Jersey

As part of a program to understand the energy-transfer and charge-transfer processes that affect ion transport through surface layers, we have studied the transmission of low energy (<10 eV) F@super -@ through ultrathin Xe films (up to several monolayers (ML)). The ions are created by electron-stimulated desorption from CF@sub 2@Cl@sub 2@-covered Ru(0001) at ~25 K, and their yields and angular distributions are measured by a digital detector with time-of-flight (TOF) capability. Our new findings include the following. (i) A strong enhancement is observed as 0.5°-1.0 ML Xe is deposited onto a fractional monolayer CF@sub 2@Cl@sub 2@ covered surface, and most strikingly, the magnitude of enhancement depends on the intensity of incident electron current. (ii) The negative ion enhancement decreases with increasing precoverage of CF@sub 2@Cl@sub 2@. (iii) The angular distribution of F@super -@ is centered along the surface normal under all conditions. These results will be discussed in terms of several different mechanisms: dielectric screening of the Xe overlayer, coupling between an anionic exciton (Xe@super *-@) and a [CF@sub 2@Cl@sub 2@]@super *-@ state, and charge transfer between a Xe@super *-@ and a F atom.

3:00pm **SS3-TuA4 Atomic Scale Femtochemistry: Electron Induced Manipulation of Single CO Molecules on Cu(111) @footnote 1@, L. Bartels, G. Meyer, K.-H. Rieder, Freie Universität Berlin, Germany; D. Velic, E. Knoesel, A. Hotzel, M. Wolf, G. Ertl, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany**

Low Temperature STM experiments on the excitation dynamics of isolated CO molecules on Cu(111) were performed. CO molecules adsorb on-top on Cu(111). By injection of electrons at a minimum sample bias of 2.4V hops of an adsorbed CO molecule can be induced. These hops either lead to the transfer of the CO onto the STM tip or to its diffusion on the sample with a probability of approx. 1:3. It was found that at constant bias the hopping rate linearly depends on the rate of electron tunneling from tip to sample (i.e. the tunneling current), thus bearing witness of a one-electron excitation at the heart of this process. However, the corresponding quantum yield of approx. 10@super -11@ is ultra-low only. Increasing the bias from 2.4V to 3.0V this rate increases. Spectroscopy with the STM reveals in the given energy range an increased density of states of CO-Cu(111) with reference to bare Cu(111). This was confirmed by two photon photoemission spectroscopy (2PPE) to correspond to the 2@pi@* level of CO. Estimating the energy barrier for CO transfer to the tip from the known CO-Cu vibrational energy, the known gap-distance and the known desorption barrier it comes out to be only insignificantly lower than the desorption barrier itself. This allows to treat this STM-induced excitation process in terms of a stimulated desorption experiment. Then the MGR-model can be applied to deduce the electron attachment rate from the net quantum yield, if an isotope effect can be found. Carefully comparing the hopping rates on mixed coverages of @super 12@C@super 16@O and @super 13@C@super 18@O an isotope effect of 2.7 can be estimated. This allows to estimate that 0.5% of the tunneling current passes through 2@pi@*. Parametrization of the isotope effect in a semiclassical model with the lifetime of the excited state and its potential slope only yields correct results, if a lifetime of the excited state of less than 3.5fs is assumed. This is in good agreement with the range of 0.8-5fs obtained by time-resolved 2PPE. @FootnoteText@ @footnote 1@ L. Bartels, G. Meyer,

K.-H. Rieder, D. Velic, E. Knoesel, A. Hotzel, M. Wolf, G. Ertl, Phys. Rev. Lett. 80, 2004 (1998)

3:20pm **SS3-TuA5 Surface Femtochemistry: Electrochemistry with Ultrafast Lasers and/or Slow Nanostructures?, J.W. Gadzuk,** National Institute of Standards and Technology

Inelastic resonance scattering of hot electrons is the fundamental mechanism underlying many electron-stimulated f-sec processes such as desorption or dissociation of molecules adsorbed on metal surfaces. The hot electrons may be produced by an ultrafast laser pulse or by a solid state tunnel device ("slow nanostructure"). Theoretical reaction rates or yields are given as an integral product of the energy distribution of the flux of incident hot electrons with the inelastic electron scattering cross section (which contains the influence of the fs intra molecular dynamics). For fixed laser fluence, the temporally narrowest pulses produce the hottest electrons. The flux of laser-generated hot electrons incident upon the surface is given by an electron-temperature-dependent expression that is akin to the oldtime Richardson equation for thermionic emission. The all important consequences of this fundamental quantum statistical mechanical constraint on our current understanding of the so-called two-temperature model of DIMET (M=Multiple) will be discussed in detail. In contrast, the incident electron flux produced by the tunnel device may be given by the (again oldtime) Fowler Nordheim equation for field emission. In either case, what is important is the energy of the incident electron relative to the energy level position of the acceptor/LUMO/negative-ion resonance of the reactant. But this is exactly one of the fundamental problems in both hardcore electrochemistry and its contemporary embodiments. Implications of the full circle linkage between venerable electron emission/electrochemistry and ultra-modern Surface Femtochemistry will also be visited.

3:40pm **SS3-TuA6 Photodesorption of Atomic Hydrogen from Si(100) at 157 nm, X.-Y. Zhu, T. Vondrak,** University of Minnesota

Irradiation of the Si(100)-(2x1):H monohydride surface by 157 nm light results in the breaking of the H-Si surface bond and the desorption of atomic hydrogen. This process can be attributed to the resonant photo-excitation of the sigma-sigma* transition of H-Si at the photon energy of 8 eV. The photodesorption cross section is 3 x 10@super -21@ cm@super 2@, independent of surface hydrogen coverage. Time-of-flight (TOF) measurement of the photodesorbed atomic hydrogen yields a mean translational energy of = 74 meV. Such a low translational energy is indicative of the short lived electronic excitation on the semiconductor surface. This short-time dynamic process is further explored by wavepacket simulation on ab initio potential energy surfaces.

4:00pm **SS3-TuA7 Study on Photon Energy Dependence of Laser-Induced Chlorine Reaction on Si(111), S. Haraichi, F. Sasaki,** Electrotechnical Laboratory, Japan

A photo-induced etching is considered as a powerful candidate of the next-generation device fabrication process from the view point of extremely low damage. However the atomic mechanism of the photo-induced surface reaction has not been well understood. We have investigated photon energy dependence of laser-induced chlorine reaction on Si(111) to elucidate the resonant reaction of this system using surface reflectance spectroscopy (SRS) and second-harmonic generation (SHG). In the SRS study, reflectance spectra from an initial oxidized, a cleaned 7x7, and a chlorinated Si(111) surface have been measured by the p-polarized light at the incident angle of around 74°, which is Brewster angle of silicon, with the photon energy ranging from 3.0 to 5.0 eV. Reflected lights themselves have a peak at around 3.4 eV involving the direct band gap transition E@sub 1@ in bulk silicon, however, the peak intensity shows no significant change due to the variation of the surface condition. On the other hand, the reflectance spectra have a peak at around 4.4 eV whose value changes remarkably due to the surface condition and is probably concerned with some surface states. The threshold laser fluency of etching reaction dependence on the photon energy ranging from 1.5 to 2.5 eV has been studied by the SHG method. The threshold fluency shows the minimum value at around 2.15 eV whose SH energy of 4.3 eV is almost equal to the above surface originated peak of the reflectance spectra. The time constant of the on- and the off-resonant reaction will also be discussed.

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4:20pm **SS3-TuA8 Photoinitiated Electron Transfer to Selected Alkyl Bromides Physisorbed on GaAs: The Effects of Alkyl Chain Length on Dissociation Cross-Sections and Fragment Dynamics**, *R.M. Osgood Jr., K.A. Khan, N. Camillone III, J.E. Moryl*, Columbia University

Brominated hydrocarbons adsorbed on semiconductor surfaces serve as ideal model systems for investigating the photoinduced chemistry of oriented molecules in the condensed phase. These adsorbates dissociate via attachment of photoexcited substrate electrons giving rise to energetic alkyl and surface-bound bromine fragments. We will describe the effect on the dissociation cross-section and fragmentation dynamics due to systematic variation of the complexity (alkyl chain length) of the adsorbate. The enhancement in the dissociation cross-section with increased chain-length will be discussed in the context of substrate-mediated dissociative-electron attachment (DEA). Comparison of these observations with those made in the gas-phase DEA of similar haloalkanes allows us to consider the role of the surface in this dissociation process. Increasing the length of the alkyl chain also leads to distinct changes in the alkyl fragment angular distributions. For methyl bromide, the angular distribution is dominated by a focused beam of hyperthermal methyl radicals at 45° (in the [-1,0] direction) from the surface normal. For ethyl and propyl bromide, inelastic scattering of the fragments results in increased importance of a slower diffuse cosⁿθ desorption. In addition, significant retention of alkyl fragments is detected by post-irradiation thermal desorption measurements. Increasing the number of degrees of freedom of the adsorbate dramatically alters the energetics of the ejection of the photofragments from the surface. Velocity distributions of the fragments clearly demonstrate that the energy partitioned into translational motion is strongly reduced when the number of rovibrational degrees of freedom is increased. Quantitative variations in the energy and angular distributions are discussed in terms of changes in energy partitioning with alkyl chain length.

5:00pm **SS3-TuA10 Surface Modification on GaAs(110) Induced by 100-3000 eV Electrons**, *B.Y. Han, K. Nakayama, J.H. Weaver*, University of Minnesota

Atomic level modification of semiconductor surfaces induced by 100-3000 eV electrons is demonstrated for the first time. Scanning tunneling microscopy results reveal that single-layer deep vacancies are created randomly on GaAs(110) terraces under conditions typical for low-energy electron diffraction and Auger electron spectroscopy. Small regrowth structures resulting from Ga and As atoms ejected onto the terrace are observed. Surface modification is related to electronic excitations, and we discuss the mechanisms in view of the rate of production of defects at various electron energies. We also discuss the consequences of this electron-induced surface modification.

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