

Surface Science

Room 326 - Session SS1-MoM

Gas-Surface Dynamics

Moderator: K.W. Kolasinski, Queen Mary, University of London, UK

8:20am SS1-MoM1 Angular Distribution of Cl Atom Products from Direct and Precursor-Mediated Hyperthermal Abstractive Chemisorption of Cl₂/Al(111), G.C. Poon, A.C. Kummel, University of California, San Diego

Resonantly Enhanced Multiphoton Ionization (REMPI) and Time-of-Flight Mass Spectroscopy (TOF-MS) have been used to demonstrate that the reaction of Cl@sub 2@ on the low work function Al(111) surface proceeds via a prompt vertical electron harpooning process. Sticking measurements were performed showing that Cl@sub 2@ adsorbs via a direct chemisorption process at either high incident translational energy or high surface temperature. However, at glancing incident angles and low surface temperatures (100 K), a precursor-mediated channel predominates. REMPI studies show that fast abstracted Cl was produced via both channels: direct, remotely-dissociated incident Cl@sub 2@, and indirect, physisorption-mediated Cl@sub 2@. An abstraction reaction results in one Cl atom bound to the surface and one Cl atom ejected back into the gas phase. For incident Cl@sub 2@ of 0.11 and 0.27 eV at 40° incident angle and 100 K surface temperature, only the precursor-mediated channel was observed with atomic Cl abstracted product energies of 0.09 to 0.14 eV. At high surface temperature, 500 K, all incident translational energies and angles yield only the direct channel, with abstracted product energies of 0.19 to 0.26 eV. Currently, angular distributions of the ejected Cl atom products are being determined for both direct and precursor-mediated channels. End-on impinging Cl@sub 2@ on the Al surface is expected to promote harpooning and subsequent abstraction products should be directed along the surface normal. Side-on physisorbed Cl@sub 2@ precursor would yield more broadly distributed abstraction products.

8:40am SS1-MoM2 Photoinduced Electron Transfer Chemistry and Dissociation of Adsorbed CO@sub 2@: Harnessing Å-Scale Molecular Acceleration Towards a Surface, R. Zehr, University of Virginia; T. Wagner, University of Essen, Germany; I. Samanta, I. Harrison, University of Virginia

Activated dissociation of molecules on a metal surface is essential to many catalytic syntheses (e.g. N@sub 2@ dissociation in NH@sub 3@ synthesis) and a firm scientific understanding of this process is important to advancing the field of heterogeneous catalysis. In commercial catalysis, activation energy barriers are invariably surmounted by random thermal energy and not through a more directed use of the energy in light, despite the ubiquitous example of photosynthesis in nature. Potential advantages of using light to overcome a rate-limiting dissociative adsorption step in catalysis include better selectivity towards a chosen reaction pathway, the ability to work at much reduced reaction temperatures, and the opportunity to exploit solar energy. Here, we present evidence that photoinduced electron transfer from a low temperature Pt(111) surface to physically adsorbed CO@sub 2@ leads to rapid acceleration of the newly formed negative ion towards the surface, neutralization, and a high energy collision with the surface that efficiently dissociates (ca. 30%) and desorbs CO@sub 2@. Importantly, this photochemical activation mechanism constitutes an Å-scale molecular accelerator that may be applicable to other hard-to-activate adsorbates. The ability to photochemically induce an adsorbate/surface collision at chemically significant energies (up to ~2.5 eV), after an acceleration over a distance of no more than a few Å from an initial configuration prescribed by the physisorption binding potential, provides novel opportunities to drive energetic dissociation and desorption processes at low temperatures and to examine the reaction dynamics of catalysis.

9:00am SS1-MoM3 Adsorption Dynamics and Desorption Kinetics of Argon and Methane on MgO(100), B.D. Kay, Z. Dohnalek, G.K. Schenter, L.R. Corrales, R.S. Smith, Pacific Northwest National Laboratory INVITED

The adsorption dynamics and desorption kinetics of Ar and CH₄ on MgO(100) are studied using a combination of molecular beam scattering and temperature programmed desorption (TPD). Both Ar and CH₄ exhibit an initial trapping probability that decreases dramatically with increasing kinetic energy and is independent of incident angle indicating adsorption is a barrier-less process obeying total energy scaling. The trapping probability for both adsorbates increases roughly linearly with the increasing coverage in the first layer. Such behavior can be described by a simple model involving constant but different trapping probabilities on clean and

adsorbate covered MgO(100) with fast intra-layer diffusion leading to preferential filling of the bare MgO(100). An alogous behavior is observed for trapping on the second and third layers and indicates layer-by-layer growth of the adsorbate overlayer with layer dependent trapping probabilities. Analysis of the TPD spectra yields desorption energies of 8.5 and 13 kJ/mol for Ar and CH₄, respectively in agreement with previous measurements and theoretical calculations. The total energy scaling observed for the initial trapping of Ar and CH₄ on MgO(100) is in sharp contrast with the normal energy scaling previously observed for these species on Pt(111). These differences indicate that the adsorbate-substrate interaction is laterally smooth on Pt(111) and highly-corrugated on MgO(100). Theoretical scattering calculations based on the classical trajectory method are used to complement and interpret the experimental data. * Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

9:40am SS1-MoM5 Adsorption of CO on Rutile (1x1)-TiO@sub 2@(110): A Molecular Beam Study, M. Kunač, Ruhr-University in Bochum, Germany; U. Burghaus, North Dakota State University

Presented are initial, S@sub 0@, and coverage dependent, S(Θ@), adsorption probability measurements, respectively, of CO on the rutile (1x1)-TiO@sub 2@(110) surface obtained along both high symmetry azimuth directions (i.e. along the [1-10] and [100] azimuth) and parametric in the impact energy, E@sub i@, the angle of incidence, and the surface temperature, T@sub s@. Whereas along the [001] azimuth approx. a Kisliuk shape of S(Θ@) has been observed, for glancing angle of incidence and E@sub i@ @>= 0.52 eV a turnover from the Kisliuk shape of S(Θ@) to an auto-catalytic adsorption (increase in S with Θ@) could be detected along the [1-10] direction. Along both azimuth directions S@sub 0@ obeys for E@sub i@ @>= 0.52 eV normal energy scaling and below that impact energy total energy scaling. The effect of an intrinsic precursor state is tentatively concluded. A decrease in the heat of adsorption with coverage indicates repulsive lateral interactions of the CO. The results will be discussed in comparison with Monte Carlo Simulations.

10:00am SS1-MoM6 Ultra-Low Coverage Spontaneous Etching and Hyperthermal Desorption of Aluminum Chlorides from Cl@sub 2@ on Al(111), T.G. Grassman, G.C. Poon, A.C. Kummel, University of California, San Diego

Non-resonant multiphoton ionization (MPI) and time-of-flight mass spectrometry (TOF-MS) have been used to monitor the desorption of aluminum chloride (Al@sub x@Cl@sub y@) etch products from the Al(111) surface at 100 K and 500 K during low-coverage (<5% monolayer) monoenergetic Cl@sub 2@ dosing. Three pulsed molecular beams of Cl@sub 2@ were prepared with translational energies ranging from 0.11 eV to 0.65 eV. The desorption products showed predominantly hyperthermal exit velocities under all dosing conditions, regardless of etch product species assignment (AlCl, AlCl@sub 3@, or Al@sub 2@Cl@sub 6@). For example, with an incident beam of Cl@sub 2@ seeded in neon (0.27 eV) at normal incidence dosing and normal detection, the etch product was found to have a most probable velocity of 532 ± 29 m/s at an Al(111) surface temperature of 100 K. This corresponds to nearly 7 times the expected thermal kinetic energy even if one assumes that the etch product is AlCl, and 30 times expected if one considers the more likely etch product, Al@sub 2@Cl@sub 6@. Sticking probability and transient etch rate profile measurements show etching even at Cl@sub 2@ coverages of less than 5% monolayer at all surface temperatures. High-temperature (500 K) etch rate profiles reach steady-state etching at equally small doses. These experimental results seem to indicate a combination of fast-time-scale surface agglomeration of the adsorbed chlorine to form aluminum chlorides, and the presence of activated aluminum chloride chemisorption states having potential energies above the vacuum level. Density functional theory calculations yield results that are consistent with both our experimental findings and mechanistic descriptions.

10:20am SS1-MoM7 Probing the Vibrational State-Resolved Gas-Surface Dynamics of Polyatomic Molecules Without the Laser, D. Killelea, D. DeSesto, R. Smith, A.L. Utz, Tufts University

We describe an experimental approach that yields vibrational-state-resolved reaction probabilities for polyatomic molecules without the need for selective laser excitation of the target state. The method relies on a detailed knowledge of the vibrational structure of the molecule under study and its vibrational energy transfer dynamics in a supersonic expansion. In the case of methane, non-equilibrium cooling of vibrational states within polyads leads to the population of a single vibrationally

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excited state under easily obtained expansion conditions, even though several excited vibrational states would contain significant population under the nominal thermal conditions of the nozzle source. We apply this approach to extract state-resolved reaction probabilities for methane in its ground vibrational state ($v=0$) and ν_4 vibrational fundamental incident on clean, low-index nickel surfaces. State-resolved reaction probabilities obtained in this way are free from the vibrational-state averaging that clouds interpretation of beam-surface reactivity measurements and permit a more direct test of theoretical models of gas-surface reactivity.

10:40am **SS1-MoM8 Kinetics of H Atom Adsorption on Si(100) at 325 - 600 K**, A. Kutana, B. Makarenko, I.L. Bolotin, J.W. Rabalais, University of Houston

The kinetics of atomic hydrogen isothermal adsorption on a Si(100) surface has been studied by the time-of-flight scattering and recoiling spectrometry (TOF-SARS) technique. A continuous decrease in saturation coverage with temperature under constant atomic hydrogen exposure has been observed for temperatures in the range 325 - 650 K. It is suggested that the obtained coverages are a result of a kinetic equilibrium between competing adsorption, abstraction, and migration reactions occurring at the surface. This approach explains how the coverages corresponding to the well-known phases of hydrogen on Si(100) at different temperatures are obtained. Introducing two types of adsorption sites into the model for the Si sticking probability, the coverage decrease is shown to be due to depletion of the surface concentration of atoms in the secondary adsorption sites. For lower temperatures, there is a significant concentration of hydrogen atoms in the precursor states that saturate the monohydride dangling bonds after hydrogen source shut-off and discontinuation of Eley-Rideal abstraction. The time for this transition is on the order of $\frac{1}{k(1 - \theta_{sat})}$, where θ_{sat} is the saturation coverage for a given temperature. Increasing the temperature leads to an increase in the migration rate from secondary to primary sites, where more efficient Eley-Rideal abstraction causes a decrease in total concentration. The migration constant k obeys the Arrhenius equation with a low activation energy of 0.29 eV. It follows from the model, and has been proven experimentally, that the saturation coverage depends not only on temperature, but also on the incoming hydrogen flux, i.e. the ambient H_2 pressure at which adsorption is performed.

11:00am **SS1-MoM9 Charge Exchange between Metal Ions and Surfaces**, X. Chen, J. Doan, University of California, Riverside; Z. Sroubek, Czech Academy of Science, Czech Republic; J.A. Yarmoﬀ, University of California, Riverside

Ion-surface charge exchange is important in surface analytical methods that employ ion beams, such as ion scattering spectroscopy (ISS), secondary ion mass spectrometry (SIMS) and electron stimulated desorption (ESD). In earlier work, we showed that the probability for neutralization of an alkali ion scattered from a metal surface is determined by the local electrostatic potential (LEP) a few Å's above the scattering site. We are now extending this work to investigate homogeneous charge exchange between metal ions and identical metal surfaces. In the first set of experiments, Ar^+ and Kr^+ ions are used to induce direct recoil of fast Al from Al(100). The neutral fraction of the recoils is then measured with time-of-flight as a function of emission angle and energy. From this data, and with the aid of Monte-Carlo simulations using scattering and recoiling imaging code (SARIC),¹ we can obtain information on homogeneous charge exchange processes. Adsorbates, such as Cs and O, will be used to modify the surface work function so that measured changes in neutralization can be used to further reveal the charge transfer process. In the next set of experiments, we are producing metal ion beams for scattering. Al ions are being produced in an $Al(CH_3)_3$ plasma, and Ga ions from a liquid metal ion source. Such pure metal ion beams will allow for simple scattering experiments in which a clear correlation between neutralization and trajectory can be made.¹ V. Bykov, C. Kim, M. M. Sung, K. J. Boyd, S. S. Todorov and J. W. Rabalais, Nucl. Instrum. Meth. B 114 (1996) 371.

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