Wednesday Morning, October 4, 2000

Surface Science Room 210 - Session SS3-WeM

Gas/Surface Dynamics

Moderator: B.D. Kay, Pacific Northwest National Laboratory

8:20am SS3-WeM1 Rainbow Scattering of Methane and Ethane Molecular Beams from a LiF(001) Surface: Dependencies on Incident Kinetic Energy and Molecular Anisotropy, *T. Kondo*, *T. Tomii, S. Yamamoto*, University of Tsukuba, Japan

An experiment to measure the angular distribution of the intensity of the alkane molecular beams scattered from a highly corrugated surface of LiF(001) has been carried out in high resolution, as a step toward the understanding of the fundamental characteristics of surface chemical reactions. One of the two major findings of the experiment shows that the rainbow peaks of the molecular beam was found to depend on its incident kinetic energy. For the clarification of this dependency, we calculated the angular distribution applying the Washboard model@footnote 1@ to fit the results by changing the amplitude of the sinusoidal corrugation in each case of different incident kinetic energy, instead of fixing the amplitude once fitted for the lowest incident kinetic energy. In this way it was further confirmed that the intensity of the rainbow peaks was reduced as the incident kinetic energy increases, contrary to the result predicted with the fixed amplitude. The reason for this discrepancy is thus because the combined structure of Li and F ions weakens the corrugation of the potential energy surface for the beam with increased incident kinetic energy. As the other major finding, the ethane molecular beam shows only one peak but not the rainbow peaks, in spite of negligible difference in the molecular size between the methane and the ethane molecules. On the other hand, the Ar atom which is heavier than both the above alkane molecules shows the distinct rainbow peaks. It is then presumed that the effect of neither the size nor the mass of the molecule is essential for the rainbow peaks. Therefore, the difference in behavior between the methane and the ethane molecules can be understood as a result of the large anisotropy of the ethane molecule. @FootnoteText@ @footnote 1@J. C. Tully. J. Chem. Phys. 92, 680 (1990).

8:40am SS3-WeM2 Probing the Extrinsic Precursor State: Methane Trapping on Ethylidyne-covered Pt(111), A. Carlsson¹, R.J. Madix, Stanford University

Under steady state conditions in catalytic reactions surfaces may be covered with stable species that affect the adsorption kinetics. It has been well documented that the adsorption probability of many molecules is facilitated by a species which can migrate across the adsorbed layer in search of a binding site. This species is referred to as an extrinsic precursor state. In order to obtain a more general understanding of this precursor state and its effect on adsorption, we have studied the kinetics of methane trapping on ethylidyne-covered Pt(111) with supersonic molecular beam techniques at surface temperatures spanning the range in which methane desorbs from the saturated monolayer and the second adsorbed layer. Because the surface is nearly saturated with ethylidyne, in order to adsorb methane must first occupy an extrinsic precursor state and then migrate to vacant sites within the ethylidyne structure to adsorb. In accordance with a precursor model for adsorption, the dependence of the adsorption probability on surface temperature gives the difference in activation energies for desorption and migration from the extrinsic precursor and the ratio of pre-exponential factors. The temperature dependence of the steady state coverage was used to determine the activation energy for conversion of the adsorbed state back into the extrinsic precursor to be 5.7 kJ/mol, compared to the desorption energy from the extrinsic precursor of about 9 kJ/mol.

9:00am SS3-WeM3 Gas-Surface Dynamics of State-Selected Reagents, A.L. Utz, L.B.F. Juurlink, R.R. Smith, C.L. DiCologero, Tufts University INVITED We use supersonic molecular beams of rovibrationally state-selected molecules to probe methane dissociation dynamics on Ni(100). These studies reveal key features of the gas-surface potential energy surface governing activated dissociative chemisorption. Excitation of the @nu@@sub 3@ antisymmetric C-H stretching vibration enhances reactivity by a factor of 1600 relative to molecules in v=0, which points to the important role of C-H stretch excitation in methane activation. The Coriolis-coupled sublevels of the triply degenerate @nu@@sub 3@ mode

differ considerably in the relative motion of the four excited C-H oscillators, but they share a similar efficacy for promoting dissociation. This observation suggests that the reactivity of @nu@@sub 3@ is likely derived from its C-H stretching character in the one C-H bond that is properly oriented for dissociative chemisorption, but not from the collective motion of all four C-H oscillators in the molecule. Rotational-state-resolved studies show that @nu@@sub 3@ reactivity varies by less than a factor of two from J=0 to 3 and provide tentative support for dynamical steering effects. Studies of other vibrational states in methane provide a dramatic example of vibrational mode specificity in a gas-surface reaction. We find that the second overtone of the @nu@@sub 4@ triply degenerate bending mode, 3@nu@@sub 4@, is at least five times less reactive than @nu@@sub 3@, despite its containing 30% more internal energy. Mode specificity establishes that a vibrationally excited molecule retains enough memory of its initial state to influence its reactivity on a metal surface. The lack of reactivity in the @nu@@sub 4@ coordinate, coupled with the absolute reactivities we measure for the @nu@@sub 3@ state, suggests that combination vibrations containing both stretch and bend excitation may be the most reactive vibrational states in a thermal sample of methane.

9:40am **SS3-WeM5 Sticking Probability Measurement of Oriented NO on Al(111),** *A.J. Komrowski*, University of California, San Diego; *B. Berenbak*, FOM Institute AMOLF, The Netherlands; *S. Stolte*, Vrije Universiteit Amsterdam, The Netherlands; *A.W. Kleyn*, Leiden University, The Netherlands; *A.C. Kummel*, University of California, San Diego

We report that by controlling the reactant orientation immediately prior to the interaction, we have gained new insight into the dissociative and abstractive chemisorption of NO interacting with a reactive metal surface, Al(111). In a novel experiment, we have used the beam reflectivity technique to measure the sticking probability of an oriented molecular beam as a function of incident molecular orientation and translational energy. We observe a higher sticking probability when the N-end is preferentially directed towards the Al(111) surface. The difference in sticking probabilities between N-end first and O-end first interactions increases with increasing incident translational energy. In contrast, Auger spectroscopy results from non-oriented molecular beams of NO with similar energies show initial surface coverage Nitrogen/ Oxygen ratios less than unity. The results are consistent with a two step chemisorption process for the initial reaction with the clean surface. First, an electron harpoons from the metal to the N-end of the molecule. The NO@super -@ molecular ion is attracted to the surface by its image charge. Second, the molecule may absorb another electron from the surface before the intramolecular bond breaks and Oxygen is deposited onto the surface while Nitrogen is ejected into the gas phase.

10:00am SS3-WeM6 Speed Distribution of Ethane Molecular Beam Reflected after Temporary Trapping on a LiF(001) Surface, *T. Tomii, T. Kondo, S. Yagyu, S. Yamamoto,* University of Tsukuba, Japan

We have measured at various scattering angles the time-of-flight of ethane molecules scattered from a LiF(001) surface of room temperature. With a high resolution cross-correlation time-of-flight technique we have successfully separated out the component of ethane molecules scattered after experiencing a temporary trapping on the sample surface. While the major peak in the time-of-flight spectrum, which consists of rotationally excited ethane molecules after single collision, can be fairly well fitted to a shifted Maxwell-Boltzmann speed distribution function, it was found that the temporarily trapped component can be reproduced by a single Maxwellian speed distribution function with a characteristic temperature lying slightly higher than the target surface temperature. This temperature tends to increase from around 300 to 600 K with the translational energy of the incident ethane beam in the range between 260 and 700 meV. The mean translational energy of the temporarily trapped molecules is almost uniform in the scattering angle, exhibiting a strong contrast to that of the directly scattered which qualitatively follows the washboard model predictions with the appropriate parameters. Despite the strong anisotropy of the ethane molecule, the directly scattered component shows a little surface rainbow features in the angular mean translational energy distribution, revealing the corrugation of the gas-surface repulsive potential. Temporarily trapped molecules are believed to be the ones which at first couple of bounces have stored their incident translational energy in the form of rotation, either cartwheel or helicopter mode, and tangential motion on a corrugated LiF(001) surface, resulting in a Maxwelllike speed distribution as a whole.

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10:20am SS3-WeM7 Trapping Dynamics of Ethane on Si(100)-(2x1) Studied by Molecular Beam Experiments and Classical Molecular Dynamics Simulations, C.T. Reeves, C.B. Mullins, University of Texas at Austin

In order to gain insight into the dynamics of trapping, or physical adsorption, we have experimentally measured the trapping probability of ethane on a clean Si(100) surface as a function of the incident translational energy and incident polar angle of the molecule at a surface temperature of 65 K using UHV molecular beam techniques. At all incident angles the trapping probability decreases as the translational energy of the incoming ethane molecule is increased from 0.05 to 1.3 eV. As the incident polar angle, with respect to the surface normal, is increased, the trapping probability decreases. This decrease in trapping probability with increasing polar angle contradicts the idea of normal energy scaling and has been seen in very few cases. Classical molecular dynamics calculations have been employed to study the cause of this unusual angular dependence. This simulation predicts trapping probabilities in good agreement with the experimental data. Analysis of the computed trajectories indicates that the initial site of impact within the unit cell, as well as the details of energy exchange during the initial impact with the surface, is important in determining the fate of an incident molecule. Although it is difficult to experimentally measure the effect of rotational energy and surface temperature on trapping, molecular dynamics simulations offer a means to study the details of these effects. Recent experimental studies by Vattuone et al. have indicated that for trapping of ethylene on Ag(001), increasing the average rotational energy from J = 2 to J = 8 can greatly decrease the trapping probability. Our simulations of ethane trapping on Si(100) have indicated that the trapping probability does decrease with increasing J, although the effect is only significant at very high values of J (>20). We have also computationally investigated the effect of surface temperature on trapping and these results will be reported.

10:40am SS3-WeM8 Dynamics of Atom Abstraction in the Scattering of NH@sub 3@@super +@ on Deuterated Al(111), *M. Maazouz*, *P.L. Maazouz*, *D.C. Jacobs*, University of Notre Dame

From a fundamental point of view, hyperthermal energy ion-surface reactions represent intriguing systems of study. The gas-surface collision energy is often high enough to drive reactions (e.g. dissociative scattering, activated chemisorption, sputtering, and atom abstraction) that are typically not observed in the thermal energy regime. Atom abstraction has been observed by many groups, yet the detailed dynamics of such hyperthermal energy reactions remain elusive. The experiment reported here examines the influence of translational energy and initial vibration quanta on the reaction of NH@sub 3@@super +@ with D/Al(111). The Al(111) surface was predosed with deuterium at 120 K, and the coverage was calibrated by TPD measurements. Resonance-enhanced mult iphoton ionization (REMPI) prepares incident ammonia ions in a specific vibration state. The ions are accelerated toward the deuterium-covered Al(111) surface at normal incidence, and the products are measured with mass-, angular-, and velocity-resolution. Specifically, the yield and kinetic energy distribution of NH@sub 3@D@super +@ is measured as a function of incident translational energy (5-80 eV) and vibration quanta (n=0-10) of NH@sub 3@@super +@.

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