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Technical Progress Report

Title: Theory of the Dissociation Dynamics of Small
Molecules on Metal Surfaces

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Our objective is to develop realistic theoretical models for molecule-metal interactions important in catalysis. The dissociative adsorption of diatomics on metals, Eley-Rideal mechanisms for recombinative desorption, and sticking on surfaces have all been examined. Efficient time dependent quantum scattering techniques have been developed to treat the molecular degrees of freedom and the thermal vibrations of the solid. In the past year, much progress has been made in the following areas:

1. Six degrees of freedom (DOF) are necessary to fully describe the dissociative adsorption of diatomic molecules, and we separate these into two groups. The most important molecular variables are r , the vibration-dissociation coordinate, Z , the center of mass translation perpendicular to the surface, and θ , the polar orientation angle of the molecule relative to the surface normal. Barrier crossing, tunneling, and the splitting of the wave function occur along r and Z , the barriers to dissociation are strongly θ -dependent, and r , Z , and θ are highly coupled during the collision. We thus represent r , Z , and θ quantum mechanically using a wave function $\psi(r,z,\theta;t)$. Surface chemistry is site and orientation specific, and it is important to include the position of the molecule over the surface plane (X,Y), and its azimuthal orientation in this plane (ϕ). However, these variables are weakly coupled to the other ones during the collision, and we treat them classically. ψ and the classical variables are propagated simultaneously many times, averaging over the initial values for X , Y , and ϕ . These are the only calculations in which all molecular degrees of freedom are included, and the necessary variables are quantum.

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A highly reactive Ni surface where direct dissociation dominates at low beam energies, and a weakly reactive Cu surface requiring high kinetic energies, were considered in one study¹. Dissociation probabilities and scattered ro-vibrational state distributions were computed as a function of beam kinetic energy for H₂ and D₂. The importance of including all DOF was demonstrated. The interaction potential tended to focus the incoming molecules into the hollow sites. Reorientation in ϕ during the reaction was also important. Much of the behavior of a given gas-metal system was shown to be determined by the way the reaction probability varied between different impact sites and molecular configurations, which cannot be described by a one barrier model. Fully classical studies were made of these systems for comparison. They did best at high beam energies (Cu), as long as the dissociation probability was sufficiently large. Various sudden approximations which reduce the dimensionality (and difficulty) of the problem were examined. Freezing the azimuthal angle ϕ was shown to lead to significant errors, while a diffractive sudden approximation (freezing X and Y) was less severe.

A second study² used our six-DOF model to examine the controversial system of H₂ on Cu, where there are questions as to the role of vibrationally excited H₂ on dissociation. Dissociation probabilities were computed as a function of initial translational energy for several ro-vibrational states of H₂. Dissociation decreased than increased with increasing rotational energy, in agreement with experiment. The results were averaged together to compute total observed dissociation probabilities for both hot nozzle and seeded beam conditions. The contributions to dissociation made by various ro-vibrational states were examined. The ground and first vibrationally excited states were found to dominate in different energy ranges. Molecular orientation during dissociation was also examined, and it was found that rotationally excited molecules were less likely to orient favorably (in θ) during the collision.

2. Several studies have been made of Eley-Rideal (ER) processes, in which a gas phase molecule reacts directly with an adsorbed species. In two earlier papers, time dependent quantum techniques were used to examine the dynamics of a gas phase H (or D) atom recombining with an adsorbed H (or D). These initial studies included only two degrees of freedom, with the atoms in a collinear arrangement perpendicular to the surface. The same

model was more recently used³ to study the reaction $\text{H(g)} + \text{Cl/Au(111)}$. It was found that a reaction was possible, although reflection of the incident H was significant due to the large mass mismatch. Reaction probabilities were examined as a function of H(g) energy and the Cl-metal vibrational state. The increase in reactivity with Cl-metal vibration leads to a temperature dependence and an apparent activation energy in agreement with several recent experiments. The product HCl was found primarily in the first excited state, also in agreement with experiments. The intermediate H--Cl-metal complex was examined with regard to lifetimes and reactive resonances. The model was also used⁴ to help understand some recent experimental studies of H(D) on D(H)/Si and Ge. Weak activation energies (temperature dependencies) and isotope effects were found.

An ER calculation including all degrees of freedom was recently completed⁵. A flat surface approximation was made in which three of the variables are conserved and three are evolved quantum mechanically. Full reactive cross-sections have been computed for $\text{H(g)} + \text{H/Cu}$, for various initial conditions. Time of flight and ro-vibrational distributions have been calculated for the product H_2 . About half of the 2.3 eV of exothermicity goes into H_2 translation, in agreement with experiment, and the rest goes into internal motion. Increasing the H-metal vibrational state increases the reactivity and the amount of internal excitation. Quasi-classical simulations lead to qualitatively similar results.

The past year has been very productive, and our progress is consistent with that outlined in the original proposal. Excellent collaborations with Mats Persson (Chalmers), Bruce Kay (Battelle), and Steve Gates (IBM) have developed. I have been spending 30% of my time on this project during the semester, and 50% during the summer. One postdoctoral associate has recently finished, and another started in September of 1993. The following papers, referenced above, have been published, accepted, submitted, or are in preparation since the last Annual Report, dated 12/17/92:

1. A. Grüneich, A. J. Cruz, and B. Jackson, *J. Chem. Phys.* 98, 5800 (1993).
2. S. Kumar and B. Jackson, *J. Chem. Phys.* (to appear 4/15/94).
3. B. Jackson, M. Persson, and B. D. Kay, *J. Chem. Phys.* (to appear 5/15/94).
4. D. D. Koleske, S. M. Gates, and B. Jackson, *J. Chem. Phys.* (submitted).
5. M. Persson and B. Jackson, (ms in preparation).

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