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Theory of the Dissociation Dynamics of Small Molecules
on Metal Surfaces: Finite Temperature Studies

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Abstract:

The goal of this study is to gain a better understanding of metal-catalyzed reactions via a detailed examination of the dynamics of molecule-metal interactions. Much effort has focused on treating the molecule as quantum mechanically as possible, and including the effects of finite surface temperature. Recently developed time dependent quantum techniques have been used to compute the dissociative sticking probability of H_2 on various metal surfaces. All molecular degrees of freedom are included either quantum mechanically or classically. The dependence upon translational and internal molecular energy, the angle and site of surface impact, and the details of the molecule-metal interaction potential were examined. Similar techniques have been used to study the Eley-Rideal mechanism for the recombinative desorption of adsorbed H atoms with gas phase H atoms. Extremely accurate methods for coupling the molecule to the thermal vibrations of the solid have been developed. They are being used in a general study of sticking, as well as to examine the trapping of H_2 and other diatomics in weakly bound molecular precursors to dissociative adsorption.

ANNUAL PROGRESS REPORT

The overall objective of this study is to develop realistic theoretical models for some of molecule-metal interactions important in catalysis. In particular, the dissociative adsorption of diatomics on metals, the Eley-Rideal mechanism for recombinative desorption, and the sticking of molecules on surfaces have all been examined. These are important steps in most catalytic processes, and are well studied experimentally. Our goal has been to treat the important molecular degrees of freedom, as well as the thermal vibrations of the solid, in a quantum fashion. Efficient time dependent quantum scattering techniques have been developed to do this. A wave function, used to describe the incoming molecule, is evolved in time via the Schrödinger Equation, scattered from or reacted with the surface, and used to compute all properties of interest. Techniques have been developed for extending these time dependent approaches to finite temperature. Much progress was made this past year in the following areas:

1. Detailed studies were made of the dissociative adsorption of H_2 and its isotopes on metal surfaces^{1,2}. These included the first calculations in which all molecular degrees of freedom were included, and the necessary variables were treated quantum mechanically². The most important molecular variables are the vibration/dissociation coordinate, the center of mass translation normal to the surface, and the polar orientation angle. Barrier crossing or tunneling and the splitting of the wave function occur along these variables, and it is important to treat them quantum mechanically, particularly for H_2 . These three variables are also strongly coupled with regard to energy exchange during the collision. We thus represent these three degrees of freedom exactly and quantum mechanically using our time dependent techniques. The other three coordinates, which describe the surface impact site and the azimuthal orientation angle were included classically, and evolved simultaneously with the quantum variables.

Two cases were thoroughly studied²: a highly reactive Ni surface where direct dissociation dominated, and a weakly reactive Cu surface where tunneling, site specificity, and molecular orientation were important. Dissociation probabilities and scattered ro-vibrational state distributions

were computed as a function of beam kinetic energy for H₂, HD, and D₂. Comparison with available experimental data was good. Fully classical studies were also made of these systems for comparison. As expected, the errors in the fully classical calculations were largest for low reaction probabilities, when tunneling and barrier transmission/reflection are important (as for Cu). Various sudden approximations which reduce the dimensionality of the problem were examined. A freezing of the azimuthal orientation angle of the molecule during the propagation was shown to lead to significant errors in many cases. A diffractive sudden approximation which conserves the center of molecular mass motion parallel to the surface was shown to be accurate for the systems studied.

2. Based on the results of our previous studies and recently developed methods for the numerical evolution of wave functions, we are implementing an improved approach to dissociative adsorption³. In addition to the vibrational and normal translational coordinate, both the polar and azimuthal orientational angles of the molecule are being treated quantum mechanically. This allows for a proper quantization of the rotational states, as well as an improved inclusion of azimuthal reorientation during dissociation, which was found to be important. A Lanczos algorithm is being tested to propagate the 4D wave function. The above diffractive sudden approach is being used, and surface impact sites are averaged over. This formulation will allow us to make a detailed and accurate comparison with the following experimentally studied systems: H₂ and D₂ on Cu(100), N₂ on W(100), and O₂ on Pt(111).

3. Many catalyzed reactions involve an incoming molecule reacting with an adsorbed radical species, with the product molecule then desorbing. We have used our time dependent quantum techniques to examine this Eley-Rideal mechanism for the case of a gas phase H recombining with an adsorbed H. Our initial study included only two degrees of freedom, with the two H atoms in a collinear arrangement perpendicular to the surface^{4,5}. Reaction probabilities and product vibrational state distributions were computed as a function of translational energy for all isotopic combinations of H and D. Large amounts of vibrational excitation were found for this very exothermic reaction, in agreement with experiment. A calculation including all six degrees of freedom is in progress⁶. A flat surface approximation is

made in which three of the variables are conserved. Thus, only three degrees of freedom need to be evolved quantum mechanically, and we are using techniques similar to those developed for dissociative adsorption to treat them. This should allow us to get full reactive cross-sections.

4. Much of our earlier work involved the extension of our time dependent techniques to include finite surface temperatures, allowing for energy transfer between the gas particle and the vibrations of the solid⁷. This will help us to explain the temperature dependence of dissociative adsorption, as well as non-reactive sticking, an important step in many surface reactions. An extremely accurate model for the trapping of very light particles was developed and tested this past year for He and Ne⁸. With the addition of rotational motion, we hope to study the sticking of diatomics in weakly bound precursor states as a function of energy and temperature.

In summary, the year has again been very productive. The work is proceeding as planned and we expect to accomplish much in the coming year. Over the past year several papers have appeared in print or have been submitted, and a number are being prepared for submission. This work was presented at recent workshops in Copenhagen and Japan, and will be discussed at invited talks at a National ACS meeting and a Gordon Conference this summer. Posters have been presented at major meetings. I have been spending about 30% of my time on this project during the semester, and about 50% during the summer. My postdoctoral associate has been working full time on this project.

Papers in print/preparation since the last Annual Report:

1. A. J. Cruz and B. Jackson, J. Chem. Phys. 94, 5715 (1991).
2. A. Grüneich, A. J. Cruz and B. Jackson, (ms in preparation; to be submitted to J. Chem. Phys.).
3. S. Kumar and B. Jackson, (to be submitted to J. Chem. Phys.).
4. B. Jackson and M. Persson, J. Chem. Phys. 96, 2378 (1992).
5. B. Jackson and M. Persson, Surf. Sci. (accepted).
6. M. Persson and B. Jackson, (to be submitted).
7. B. Jackson, J. Chem. Phys. 94, 5126 (1991).
8. B. Jackson, (ms in preparation; to be submitted to J. Chem. Phys.).

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