

## **Theoretical Chemistry**

Our group's research focuses on theoretical and computational studies of molecular structure and dynamics. Most of our work involves a mix of pencil-and-paper calculations and computer calculations; the precise balance between these two depends on the project and on a student's particular interests. Our group Web site (see above) has references to recent papers and preprints that discuss some of our recent projects.

### **1. Spectroscopic properties induced by weak molecular interactions**

Isolated hydrogen molecules in the gas phase are infrared (IR) inactive; however, in the solid phase, interactions between neighboring molecules give rise to weak transition dipole moments that ultimately generate a beautiful (and complicated) IR absorption spectrum. One of the most fascinating conclusions arising from experimental studies of this spectrum is that H<sub>2</sub> molecules in the solid have "good" rotational and vibrational quantum numbers. No other molecular solid exhibits this property.

Another important feature of solid hydrogen is that the individual molecules in the crystal undergo large-amplitude quantum mechanical zero point motions; solid hydrogen is therefore termed a "quantum crystal". The IR spectrum of solid hydrogen can only be understood quantitatively if these zero point motions are taken into account.

We are investigating how the IR spectrum of solid hydrogen is affected by the presence of chemical impurities dissolved in the solid; these studies tell us about the physics of solvation in cryogenic quantum solids. The impurities that are of interest include rare gas atoms (Ar, Kr, Xe) and the small molecules HCl, N<sub>2</sub>, and CO. This work involves close collaboration with experimentalists at the Air Force Research Laboratory (Eglin AFB, FL) and at the University of Wyoming. Students working on this project will gain experience with ab initio quantum chemical methods and with computational methods for solving many-body Schrodinger equations.

### **2. Dynamics of adsorbates on insulator surfaces**

In a collaboration with the Larese research group, we are investigating the rotational dynamics of small molecules (such as CH<sub>4</sub> and H<sub>2</sub>) adsorbed on crystalline insulators (primarily NaCl and MgO crystals). These insulators are ionic solids, and the ions exposed at the crystal's surface generate strong electrostatic fields that orient the adsorbed molecules in specific directions. The net effect is to perturb strongly the rotational energy levels of the adsorbed molecules. The Larese group studies these perturbations experimentally using inelastic neutron scattering techniques.

Our group attempts to relate the observed rotational energy level spectrum to the electrostatic fields present at the surface by solving the rotational Schrodinger equation for the adsorbate molecules. We compare the rotational energy level spectrum generated by various

model fields with the spectrum observed experimentally, and through this comparison learn about the electronic structure of the surface layer of the crystal.

This research has important technological and environmental ramifications because metal oxide surfaces such as MgO are used extensively as catalysts for industrial air purification. By studying the dynamics of small adsorbates on these surfaces, we can gain atomic-level insight into the electronic structure of the surface and learn how these materials function as catalysis. Students working on this project will gain experience with ab initio quantum chemical methods and with computational methods for solving the rotational Schrodinger equation.

### **3. Dynamics of gas phase chemical reactions and gas–surface collisions**

We have a long-standing interest in the dynamics of elementary gas phase chemical reactions that are important in planetary atmospheres or in interstellar environments. At present, our main focus is on interstellar collisions between rovibrationally excited H<sub>2</sub> molecules and light atoms such as H or He. These collisions provide a mechanism for cooling hot clouds of H<sub>2</sub> molecular gas, which allows these clouds to condense under the influence of their self-gravity to form young stars. Students working on this project will perform classical and quantum mechanical simulations of these collisions using existing ab initio potential energy surfaces, and from these simulations will determine which regions of the potential energy surface are most critical for describing the collision dynamics. They will then attempt to improve the existing potential energy surfaces in these areas by performing ab initio quantum chemical calculations for the collision system.

More recently, we have begun to study the dynamics involved when gas flows impinge on heated solid surfaces. Of primary interest is how the atoms and molecules in the gas carry heat away from the surface. When a cold gas atom collides with a hot surface and rebounds away from it, the principle of conservation of momentum dictates that the hot surface receives a small forward thrust to compensate for the gas atom's increase in backward momentum. This principle is at the heart of proposed next-generation micropropulsion systems for satellites in Earth orbit. The aeronautical engineers who will design these micropropulsion systems need accurate dynamical information that characterize atom–surface collisions at the atomic scale. Our goal is to provide this information by performing molecular dynamics simulations of gas–surface collisions. Students working on this project will perform classical mechanical simulations of gas–surface collisions using model potential energy surfaces, and may also perform some quantum chemical calculations of gas–surface interactions.