Tuchler Group Research Projects

Gas phase equilibrium constants: Equilibrium constants are important for modeling equilibrium composition of mixtures for systems such as that of the atmosphere or in smokestacks, in calculating theoretical performance of rocket combustion chambers (in which equilibrium is established very quickly), or in determining absorption coefficient when a competing absorber that is in equilibrium with the molecule of interest is present and must be accurately accounted for. In addition, the temperature dependence of the chemical equilibrium constant contains thermodynamic information about the free energy, the entropy, and the enthalpy of the overall reaction. Thus reliable experimental data regarding these constants is necessary. Unfortunately, such data is often difficult to acquire, especially under conditions that are similar to those in which the process of interest occurs.

Experimental method: A relatively simple technique for determining the gas phase equilibrium constant is by measuring of the change in absorption as a function of the total cell pressure or by measuring the change in path length required to achieve the same absorption at two different pressures.[1, 2] To achieve this with relative ease and large dynamic range, our experiments rely on a Cavity Ringdown Absorption Spectrometer (described below). This spectrometer is housed in a gas cell that was designed with an insulating jacket, through which liquid can be flowed. Because we can control the temperature of the liquid over a range of -50 to100 C, we can determine temperature dependence of the equilibrium constant by measuring the equilibrium over a range of temperatures.

Cavity Ringdown Absorption Spectroscopy: CRAS is a simple, ultra-sensitive absorption technique that may be utilized for a variety of research projects and physical chemistry laboratory experiments. Briefly, CRAS is little more than a tunable laser, two high reflectivity confocal mirrors, a cell containing the molecular species of interest, and a sensitive, stable diode detector. In application, ~1 mJ of light from a tunable wavelength, pulsed laser is directed into the back of one of the high reflectivity mirrors (Step 1 in fig.1). The small amount of light that is transmitted into the cavity is trapped for a period of time that is a function of the mirror reflectivity (Step 2 in fig. 1). A photoelectric detector measures the rate of decay of light from the cavity and the signal is stored in a digital oscilloscope (Step 3 in fig. 1)

There is a characteristic rate of decay for the empty cavity that is a function of wavelength. The rate of decay increases when there is an absorber present. The amount of change is related to the intensity of absorption. Because the spectrometer operates within the Beer's Law limit, it has a sensitivity that is directly related to the effective path length of the light. With a cell length of 1m and a mirror reflectivity of 99.995%, we expect an effective path length of ~10,000 m. In addition, CRAS is independent of laser power, as it measures only the rate of decay of light injected into a cavity. Thus CRAS is a sensitive, accurate analytical technique for determining, among other things, relative concentration of a species.

Equilibria of Interest: The first application of our experiment is revisiting the well established $2NO_2 \rightleftharpoons N_2O_4$ equilibrium constant at room temperature. Following this demonstration of principle experiment, we will vary temperature of the cell controllably over the range of -50 C to 100 C with a Thermo Neslab RTE-740 refrigeration and heating circulator. By measuring the equilibrium constant at various temperatures, we will determine the various

thermodynamic constants associated with this reaction. Calculations indicate that we should have no difficulty in measuring equilibrium constants whose value ranges over at least 6 orders of magnitude using CRAS and the proposed cell.

Following the studies on NO_2, we will measure the equilibrium constant of the less well studied system, $2\,HX \rightleftharpoons H_2 + X_2$ ($X = Cl$ or I). Because of the corrosive nature of HI and possible etching of the mirrors, the system will be studied under flow conditions.
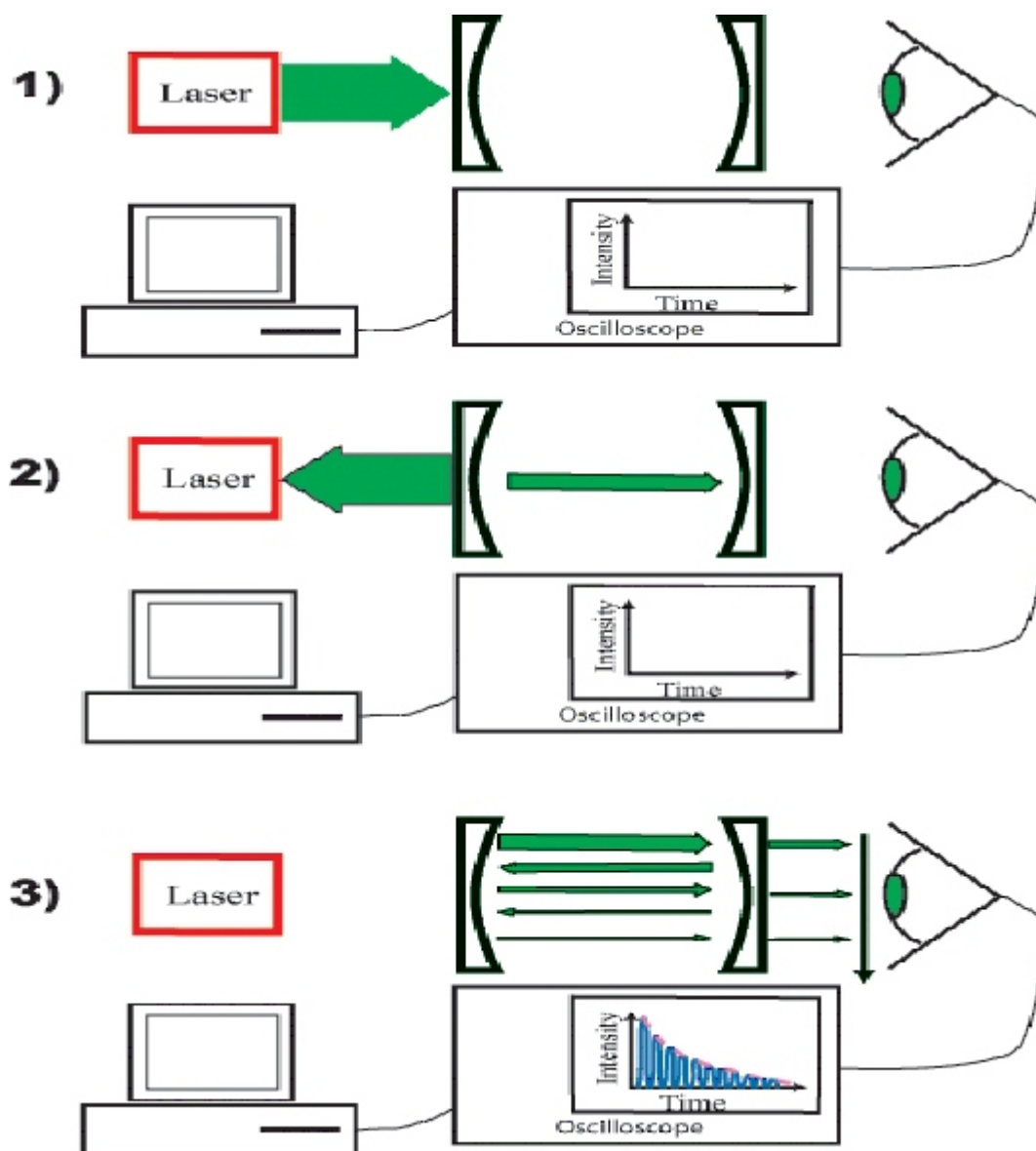

Figure 1

Nodal structure of highly vibrationally excited small molecules in the gas phase: A second project in which I am interested is *directly* identifying the quantum structure of vibrationally excited small molecules. Such structure, while assumed based on quantum theory and indirect experimental evidence, has been observed directly only once[3] and is important for researchers working with photoexcitation of highly vibrationally excited molecules, including ultrafast and frequency resolved studies of (i) intermolecular energy transfer[4] and (ii) unimolecular and bimolecular reaction dynamics, including bond-selective photochemistry. In addition to addressing experimental issues of significance to the broader physical chemistry/chemical physics community[5], the project addresses fundamental quantum properties of molecules in energy and internuclear separation regions that are critical for our understanding of the very complicated dynamics of reactions that must pass through regions of strong coupling in which the adiabatic approximation breaks down.

Experimental method: Briefly, as shown in figure 2, the vibrational wave- function, ψ_a, is prepared with a photon, λ_1. ψ_a extends much further along the internuclear coordinate than that of the ground vibrational state, ψ_0.[6] The relatively large spatial extent of $|\psi_a|^2$ depicted in the figure facilitates transitions to a repulsive surface at wavelengths, λ_2, which are significantly longer (red shifted) than those needed at the equilibrium geometry, i.e., λ_3. In fact, when excitation is to a repulsive surface, the transition strength is expected to be maximum at the outer turning points, if for no other reason than the probability density is very large at these points. It is thus clear that a repulsive electronic surface can be accessed by photons whose combined energy is far less than that necessary for transitions which originate from the equilibrium geometry of the ground vibrational state. By varying λ_2, the $\psi_b \leftarrow \psi_a$ absorption spectra will be determined and will identify the nodal structure
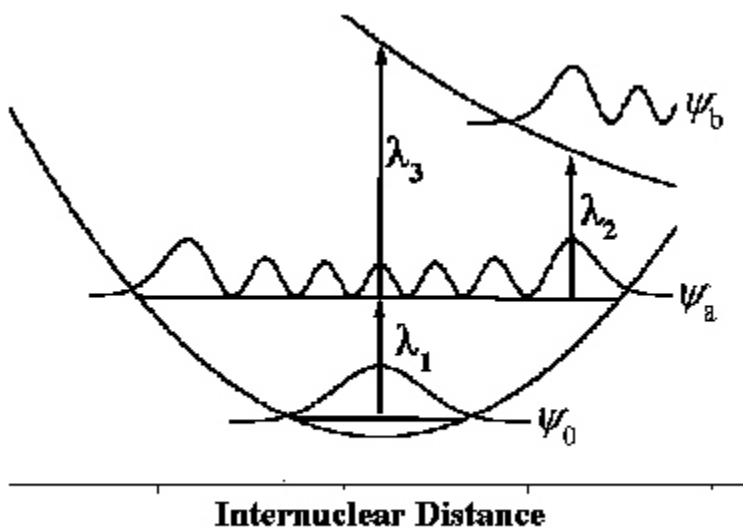

Internuclear Distance

Figure 2

of ψ_a. Again, this concept has been demonstrated nicely by the work of Crim and coworkers in their study of the $|04>^-$ local mode level of H_2O.[7] Our experiment differs from theirs, however, in that we will work in a gas cell (not a molecular beam), we will use visible radiation (not UV-radiation), and we will monitor relative absorption strength via chemiluminescence intensity (not

using multi-photon ionization techniques).

      Molecules of Interest: Experimentally, the first molecules that I will study are H_2S, HCl and HBr. All of these molecules have well studied ro-vibrational structure that resides in an energy region that is easily accessible with a tunable, visible lasers.[8,9] In addition, to my knowledge no overtone spectrum of HBr have been reported at wavelengths shorter than 700 nm. The highest overtone reported, $6 \leftarrow 0$, has a band center at 14,004 cm^{-1}.[7] Certainly, CRLAS will equip me with an excellent tool with which to search for the $7 \leftarrow 0$ overtone.

      Associated theory projects: Quantum mechanics shows us that the form of the potential describing the system determines the form of the wavefunctions.[10] Similarly, the wavefunction contains all information available regarding the system at a given energy, including information about the potential. With this in mind, a student of mine created a software package based on a simple, analytical, finite difference algorithm, that accepts a one dimensional potential as input and provides a wavefunction as the output.[11] Remember that it is such a wavefunction that our experiment will probe. Ultimately my intent is to involve a student at Holy Cross in upgrading the software so as it can be used to model the experimental data by varying the potential to fit the data. This approach is standard and is similar to working a problem backwards...having the solution and trying to identify the problem.

      Interestingly, significant discussions with Professor Tom Williams in the physics department leads me to believe that we will be able to work the problem in the forward direction as well. In other words, the form of the experimentally determined wavefunction (the "question") will be used to determine the form of the potential (the "answer") within a narrow energy range.[12] This past summer, Professor Williams and I worked to apply this algorithm to model systems and to existing experimental data on water with promising results. I expect to continue my collaboration with Professor Williams on this project while at Holy Cross.

Student involvement: Students have played an active role in developing all parts of the experimental apparatus and in developing the experiments proposed in my NSF grant. Everything from design of the gas cell and alignment rods to development of the pedagogical experiments and the data acquisition protocol has students' signatures on them. I perceive such student involvement is a very important component of my research that will continue.

1. Harris, Louis; Kenneth L. Churney; *J. Chem. Phys.*, **47**(1), 1703 (1967).

2. Nordstrom, Robert J.; Walter H. Chan; *J. Phys. Chem.*, **80**(8), 847 (1976).

3. F. Flemming Crim, *Acc. Chem. Res.*, **32**(10), 877 (1999); F. Flemming Crim, *J. Phys. Chem.*, **100**(31), 12725 (1996).

4.George W. Flynn, Charles S. Parmenter, Alec M. Wodtke, *J. Phys. Chem.*, **100**(31), 12817 (1996).

5.Briefly, the field of chemical reaction dynamics is directed toward a focused, detailed exploration of molecular reactivity and the chemical reaction. This involves a quantum or semi-classical description of the reactive event.

6. M.S. Child, L. Halonen, *Adv. Chem. Phys.*, **57**, 1 (1984); M.S. Child, *Acc. Chem. Res.*, **18**, 45 (1985).

7. R. L. Vander Wal, J. L. Scott, and F. F. Crim, *J. Chem. Phys.*, **94**(3), 1859 (1991); F. F. Crim, *Ann. Rev. Phys. Chem.*, **44**, 397 (1993).

8. Nobuo Nishimiya, Tokio Yukiya, Tomoaki Ohtsuka, Masao Suzuki, *J. Mol. Spec.*, **182**(2), 309 (1997).

9.J.-M. Flaud, O. Vaittinen, A. Campargue, *J. Molec. Spectrosc.* **190**, 262 (1998)., O. Vaittinen, L. Biennier, A. Campargue, J-M Flaud, L. Halonen, *J. Molec. Spectrosc*. **184**, 288 (1997).

10.Any quantum mechanics text will contain examples of generating a wavefunction based on a given potential, e.g., particle in a 1-D well, harmonic oscillator, hydrogen atom. See, Ira N. Levine, Quantum Chemistry, 5th edition (Prentice Hall, Upper Saddle River, NJ) 2000.

11.Chris Lue and Matthew Tuchler, "The 1-D Schrodinger Equation Black Box: A Virtual Instrument for Teaching and Research", Poster for the American Chemical Society Meeting in Chicago, 2001

12. H. Thomas Williams, *"Superpostition Solutions to the Schodinger Equation"*, accepted for publication, *Am. J. Phys.*, summer, 2002.