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TECHNICAL PROGRESS REPORT

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THE PHOTODISSOCIATION AND REACTION DYNAMICS OF VIBRATIONALLY EXCITED MOLECULES

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INTRODUCTION

We have directed our Department of Energy supported research along three lines, all leading toward the goal of studying the dissociation and reaction dynamics of highly vibrationally excited molecules in new detail, during the last year. We have used the combination of vibrational overtone excitation and laser induced fluorescence detection to study the dissociation dynamics of hydroxylamine (NH_2OH), have performed our first laser induced grating experiments on water, and have begun assembling a new apparatus for preparing vibrationally excited molecules with simulated Raman excitation. We study the role of vibrational excitation in photodissociation dynamics by using a vibrational state preparation technique, such as vibrational overtone excitation or stimulated Raman excitation, to create molecules with particular nuclear motions and then to excite that molecule to a dissociative electronic state. Because the vibrational excitation alters the dissociation dynamics in the excited state, both by providing access to different portions of the excited state surface and by altering the motion of the system on the surface, we usually refer to it as vibrationally mediated photodissociation.

VIBRATIONALLY MEDIATED PHOTODISSOCIATION OF HYDROXYLAMINE

Hydroxylamine (NH_2OH) is an intriguing molecule for testing ideas that we have developed about vibrationally mediated photodissociation. It has a relatively weak H_2N-OH bond (256 kJ/mol) and two different types of bonds (N-H and O-N) that are likely candidates for vibrational overtone excitation. Our plan for exploring its vibrationally mediated photodissociation dynamics is to obtain its vibrational overtone absorption spectrum, using photoacoustic spectroscopy, to study its single photon photodissociation, and to observe its vibrationally mediated photodissociation for excitation of both the O-H and N-H bonds. We are far along in this study, having obtained much of the data for the vibrationally mediated photodissociation with excitation of the O-H bond.

The photoacoustic spectra in Figure 1 illustrate an intriguing aspect of hydroxylamine. The figure shows the spectra for excitation in the vicinity of the second ($3\nu_{OH}$), third ($4\nu_{OH}$), and fourth ($5\nu_{OH}$) overtones of the O-H streching vibration. The spectra for the second and third overtone vibrations have sharp, albeit congested, rotational structure. The spectrum for the fourth overtone vibration has none. Simulating the spectra as those of an asymmetric top with predominantly an *a*-type rotational contour having a small *b* or *c*-type contribution reproduces the rotational structure quite well *provided* we assign a linewidth of 0.5 cm^{-1} in the case of $3\nu_{OH}$ and 1 cm^{-1} in the case of $4\nu_{OH}$. Both of these widths exceed the bandwidth of the dye laser and clearly reflect couplings within the molecule. The situation in both the experiment and simulation is dramatically different for $5\nu_{OH}$, where we must use a linewith of 10 cm^{-1} to reproduce the spectrum. Although the fourth overtone region lies below the dissociation threshold for NH_2OH, the coupling apparently changes dramatically between $4\nu_{OH}$ and $5\nu_{OH}$. Our goal now is to probe the vibrationally mediated photodissociation dynamics for molecules excited in these different regions by measuring the distributions of the products among their quantum states. (Indeed, we have much of the single photon and vibrationally mediated photodissociation data in hand.)

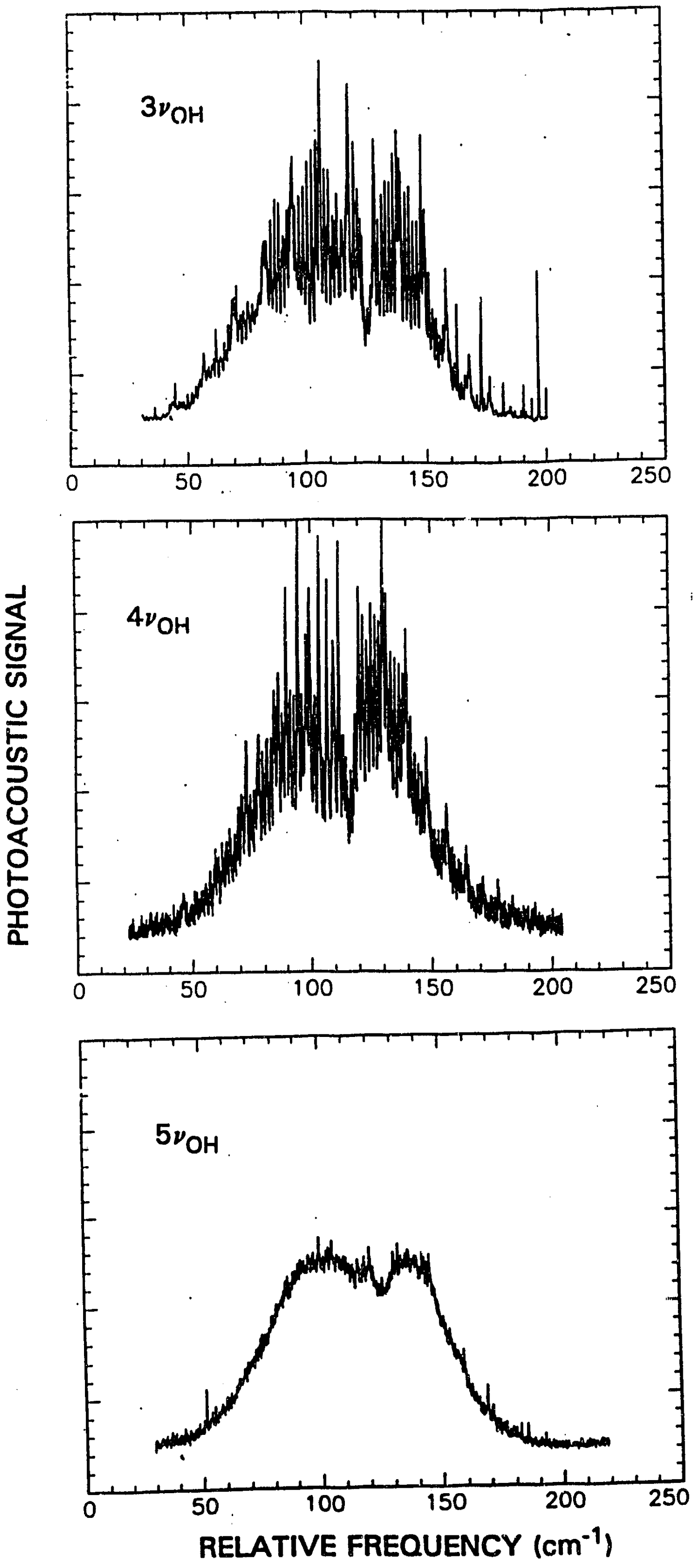

Figure 1 Spectra of NH_2OH in the region of the second, third, and fourth overtone vibrations.

We have also begun calculations based on *ab initio* potential energy surfaces to explore these vibrational dynamics. After obtaining a number of points on the potential energy surface, we have calculated the vibrational eigenvalues and used them to predict the evolution of excitation initially deposited in the O-H stretch. Fast decay from this state translates into a large linewidth in our spectra. In these first calcuations, the states $3\nu_{OH}$ and $4\nu_{OH}$ live a very long time, consistent with their relatively narrow lines, while $5\nu_{OH}$ decays in a fraction of a picosecond, consistent with its broader lines. Hydroxylamine is not a particularly convenient molecule to handle experimentally, but its fascinating dynamics make it worth the effort. We believe that NH_2OH is showing us interesting experimental behavior that will yield to good theoretical interpretation.

LASER INDUCED GRATING SPECTROSCOPY

The basic approach of a laser induced grating experiment is to form an interference pattern in a sample by crossing two identical excitation beams, obtained by splitting a single laser beam into two parts, and to probe it with another beam that diffracts from the resulting grating. The interfering excitation beams create a grating pattern with regions of excited state population separating regions with no excited molecules, corresponding to maxima and minima in the interference pattern. The probe beam diffracts from these regions if the excited state prepared by the excitation beam has a different index of refraction at the probe wavelength than the ground state. This approach is well established for liquids and has been demonstrated in gases, but its application to detecting highly vibrationally excited states has just begun.

The simplest laser induced grating measurement we are performing creates a grating with the vibrational overtone excitation light and probes it with ultraviolet light in a transition to the electronically excited state. This corresponds to the first two steps in vibrationally mediated photodissociation, but diffraction of the probe beam, not the formation of a photofragment, signals the transition to the electronically excited state. Hayden and coworkers have pioneered this approach in highly vibrationally excited water vapor. They excite the $|04\rangle^-$ state with interfering vibrational overtone excitation beams and probe the excited state by diffraction of 266-nm light, which makes a transition from the vibrationally excited state to the dissociative electronically excited state. The larger cross section for electronic excitation of the vibrationally excited molecule compared to the ground vibrational state molecule at the selected wavelength produces the difference in index of refraction between the maxima and minima in the grating that diffracts the probe light. Varying the wavelength of the excitation laser produces the vibrational overtone excitation spectrum of water.

We have learned the details of laser induced grating spectroscopy with experiments on NO, using a two-photon excitation, and with experiments on water, using vibrational overtone excitation. We have the methodology well in hand, have reproduced the earlier measurements of the vibrational overtone excitation spectrum of the $|04\rangle^-$, and are preparing to study other vibrational states such as $|13\rangle^-$. The most intriguing possibility for this technique is obtaining the ultraviolet excitation spectrum out of different vibrational states. We have already shown that this spectrum has structure that reflects the nodal structure of the vibrationally excited state and the dissociating state. Implementing laser induced grating spectroscopy will allow us to obtain these spectra easily and sharpen our comparision with detailed theoretical calcuations.

STIMULATED RAMAN EXCITATION

Our newest development effort is the use of stimulated Raman excitation as a preparation technique. Stimulated Raman excitation (SRE) is a two-photon scheme that is potentially versatile in the types of vibrations prepared but cannot produce the high levels of excitation possible with vibrational overtone excitation and stimulated emission pumping. Stimulated Raman excitation uses two photons whose difference equals a fundamental vibrational frequency to transfer molecules from the ground vibrational state to that excited level. This technique can move a substantial number of molecules, approaching saturation in particularly favorable cases, and has proven itself for state preparation in vibrational energy transfer and bimolecular reaction experiments. An injection seed Nd:YAG laser and a new dye laser are crucial components of these stimulated Raman experiments. We are in the midst of obtaining the hardware and have begun construction of the ancilliary components of the measurements.

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