

# Spectroscopic Probes of Vibrationally Excited Molecules

at  
Chemically Significant Energies

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Progress Report  
for Period August 15, 1992 - August 14, 1993

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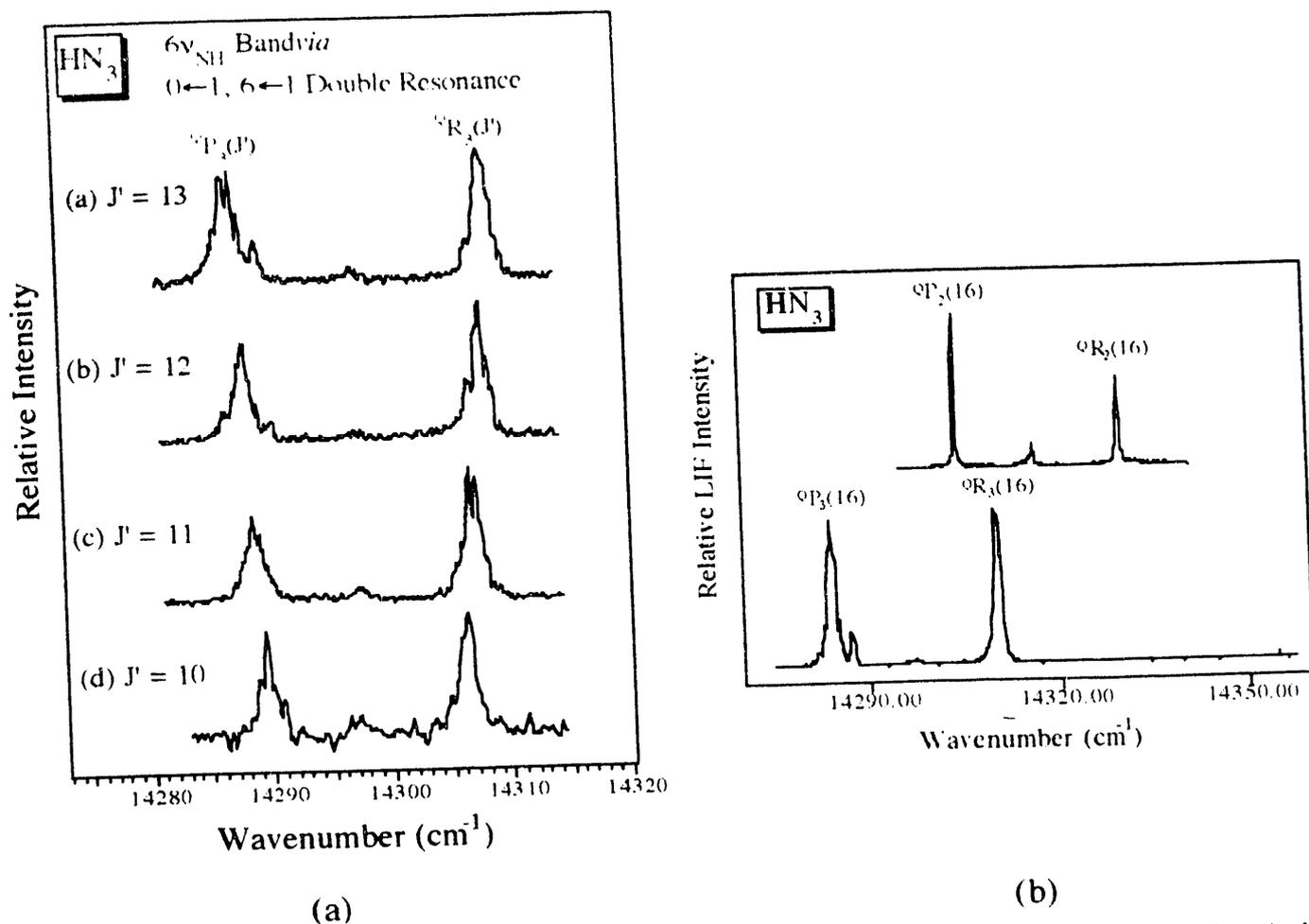
## **Project Overview**

These experiments apply multiple-laser spectroscopic techniques to investigate the bond energies, potential surface topologies, and reaction dynamics of highly vibrationally excited molecules. Two major goals of this work are: 1) to provide information on potential energy surfaces of combustion related species as well as other small molecules at chemically significant energies, and 2) to test theoretical models of unimolecular reaction rates critically *via* quantum-state resolved measurements.

## **Recent Progress**

### **Unimolecular Dissociation Dynamics of $\text{HN}_3$**

In the last year we have been applying infrared-optical double resonance to investigate the unimolecular dissociation dynamics of hydrazoic acid ( $\text{HN}_3$ ). Our infrared-optical double resonance studies of this molecule have been aimed at determining: 1) the precise threshold for producing  $\text{NH}(^1\Delta)$ ; 2) the height of the barrier on the singlet surface; 3) the geometry of the molecule at the transition state; and 4) the nature of the coupling of the NH stretch vibration to the other vibrational modes of the molecule. All of this information can be extracted from the combination of infrared-optical double resonance photofragment excitation spectra, which determines precisely the  $\text{HN}_3$  reactant energy, and LIF spectra of the resulting NH fragments, which determines the product internal energies. The first step in this process, which we have recently completed, involves assigning the double resonance overtone spectra. The assigned spectra in Fig. 1 demonstrate our ability to prepare  $\text{HN}_3$  molecules in selected rotational states of the the  $6\nu_{\text{NH}}$  level.



**Figure 1.** Series of  $6\nu_{\text{NH}}$  vibrational overtone excitation spectra of  $\text{HN}_3$  recorded by infrared-optical double resonance photofragment spectroscopy. (a) Transitions to states in  $6\nu_{\text{NH}}$  with  $K=3$  and  $J=9-14$ ; (b) Comparison of transitions to states with  $K=2$  and  $K=3$  in  $6\nu_{\text{NH}}$ .

We are in the process of determining the *threshold* for producing singlet NH products by observing how high in  $J$  and  $K$  we must excite the  $\text{HN}_3$  reactant before the singlet channel opens. We will determine the *barrier* on the singlet surface by combining our knowledge of the reaction threshold on that surface with measured internal state distributions of the singlet NH products.

In the coming year we plan to complete our work on  $\text{HN}_3$  and apply infrared-optical double resonance spectroscopy to examine the unimolecular reaction dynamics of HONO. The HONO molecule can exist in *cis*- and *trans*- forms and is a prototype system for isomerization reactions. We plan to use

infrared optical double resonance to probe the dynamics of unimolecular isomerization at the  $v=1$  and  $v=2$  levels of the OH stretch.

### **Extension of Double Resonance Techniques to Small Free Radicals**

We have begun work in the last year to determine the feasibility of extending our infrared-optical double resonance photofragment spectroscopy technique to small free radicals. This approach should allow the precise determination of chemical bond energies of these transient species. We plan to generate free radicals, such as HCO, by photolysis of suitable precursors. Because the concentrations of radicals is expected to be low, we need to greatly increase the sensitivity of our technique. Moreover, we need to extend the range of dissociation products that we can detect spectroscopically. In particular, dissociation of small radicals often result in the generation of atomic fragments. Spectroscopic detection of atoms is in principle much more sensitive than LIF detection of diatomics and triatomics insofar as there is no partitioning of the fragments among internal states.

Over the last several months we have been developing the ability to monitor atomic dissociation fragments *via* laser induced fluorescence in the VUV region of the spectrum. VUV light will be generated by frequency tripling in a low pressure xenon cell, and we have just recently completed construction of a new reaction chamber that is equipped with this capability. Over the next several months we plan to carefully characterize the VUV generation process as well as the increased detection sensitivity achieved by doing LIF on atoms. We will then begin to apply this approach as a detection scheme for double-resonance photofragment spectroscopy of photogenerated free radicals.

**Statement of Unexpended Funds**

By the end of the current budget period (August 14, 1993), I anticipate having leaving less than 10% of the budgeted funds unexpended.

*Thomas O'Connell*

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