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COLLISIONAL ENERGY TRANSFER IN HIGHLY VIBRATIONALLY  
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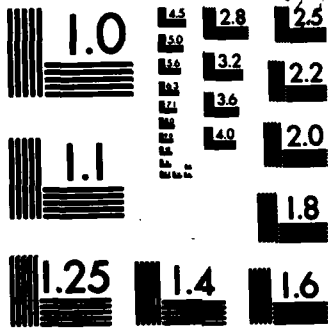
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## 18. SUPPLEMENTARY NOTES

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Energy transfer, rotational relaxation, laser, hydrogen fluoride, deuterium fluoride.

## 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Overtone vibration-laser double resonance measurements have provided new data on vibrational and rotational relaxation in HF( $v=2$ ). These experiments determine the magnitudes of the total vibrational relaxation rate constants for HF( $v=1$  and  $2$ ) as well as their temperature dependences. Detailed analysis yields the variation of the branching between competing V-V and V-TR pathways. Rotational relaxation data come from these measurements as well. The temporal

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evolution of individual rotational states observed in the double resonance studies provides level-to-level energy transfer rate constants when analyzed using an iterative fitting scheme which incorporates scaling relations among the rate constants.

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COLLISIONAL ENERGY TRANSFER IN HIGHLY VIBRATIONALLY EXCITED MOLECULES

(Contract No. N00014-79-C-0415)

1. Principal Investigator:

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Associate Professor  
Department of Chemistry  
University of Wisconsin  
Madison, WI 53706

2. Contract Description:

The aspect of this work funded by the Office of Naval Research is the direct measurement of rotational relaxation rates of highly vibrationally excited hydrogen fluoride and deuterium fluoride. We expect to uncover systematic trends related to the initial rotational level of the excited molecule and to discover the influence which vibrational excitation has on rotational relaxation processes.

3. Scientific Problem:

Little experimental information is available on rotational energy transfer processes in general, and virtually none exists on the behavior of rotations in highly vibrationally excited molecules. This study will provide some of the first detailed data on rotational relaxation of molecules with large amounts of vibrational energy. As discussed below, the preparation technique and final state analysis are highly specific, so that the resulting rates represent an average over only the thermal rotational and translational energy distribution of the ground vibrational state collision partners. The rates come from a direct (time resolved) measurement of the populations of individual rotational states. Excitation of different vibrational states provides information on the influence which vibrational excitation

has on rotational relaxation rates, and produces new vibrational relaxation data, also. Our measurements will be valuable for comparison to inferential techniques, such as overtone vibration linewidth measurements, and as a test of promising theories based on modified forms of the sudden approximation. These experiments on important but as yet unexplored rotational relaxation in highly vibrationally excited molecules promise to produce unique, detailed data which extend our fundamental and practical understanding of energy transfer dynamics and test theoretical models of these processes.

4. Scientific and Technical Approach:

The detailed measurements of this study require two essential experimental capabilities: (1) preparation of a single rotational state in highly vibrationally excited molecules and (2) temporally resolved detection of the populations of other rotational levels. We prepare the desired state by direct excitation of a molecule from its ground vibrational state to an overtone vibrational level using visible photons from a pulsed dye laser or near-infrared photons produced by stimulated Raman scattering of the dye laser pulse in hydrogen gas. Because this excitation scheme relies on small transition probabilities arising from anharmonic terms in the potential and nonlinear terms in the dipole moment expansion, only a small fraction of the molecules are excited. We have demonstrated, however, that this is adequate for vibrational relaxation measurements on HF( $v = 3, 4, 5$ ). (Chem. Phys. Letters 71, 258 (1980) and J. Chem. Phys. 74, 4455 (1981) and 75, 3871 (1981.)) The short pulse duration ( $\sim 6$  ns) of our Nd:YAG/dye laser is essential to our measurements of the temporal evolution of individual rotational levels. The detection scheme employs

laser double resonance to probe a single rotational state in the vibrationally excited molecule. The exciting laser pulse and infrared probing radiation from a continuous HF(DF) laser propagate collinearly through a long (~ 1m) cell where transient absorption of the probe radiation mirrors the temporal evolution of an individual rotational state. After the cell, the preparation beam and probe beam are separated, and the intensity of the probe beam is recorded by a fast infrared detector and transient digitizer. A multichannel analyzer and computer accomplish the requisite signal enhancement, and analysis of the signal amplitude and form provides relaxation rates. The exciting laser selects a single vibrational-rotational level, while the probe laser interrogates an individual state also.

The specificity of excitation and detection is an essential feature of the experiment. Using this technique we can explore rotational energy transfer in HF(DF) in different vibrational levels at a variety of temperatures and with many different collision partners. These experiments provide rotational energy transfer rate constants and help to uncover the mechanisms of energy transfer. They also test theoretical descriptions of inelastic collisions in polar molecules.

#### 5. Progress:

During the past year, we have continued to apply our overtone vibration-laser double resonance technique to both vibrational and rotational energy transfer measurements in HF( $v=2$ ). The vibrational relaxation studies have determined the total vibrational energy transfer rate constants for HF( $v=1$  and 2) and shown that approximately 60% of the relaxation occurs by a V-V mechanism (J. Chem. Phys. 77, 3974 (1982));

78, 6344 (1983)). We have used our heated double resonance cell to determine the temperature dependence of the rate constants for vibrational energy transfer in HF( $v=1$  and  $2$ ). The rate constant for  $v=2$  is unique in that it shows a markedly slower decrease with increasing temperature than  $v=1,3,4$ , or  $5$ . This seems to reflect the importance of V-V energy transfer for HF( $v=2$ ). Detailed analysis allows us to extract the temperature dependence of the V-V process along with that of the V-TR process. Higher pressure measurements are now providing unique data on HF dimer relaxation of HF( $v=1$ ). The preliminary value of the rate constant  $k_1^D \sim (8 \pm 3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  shows that relaxation by dimers is about 50 times more efficient than relaxation by the monomer.

The rotational relaxation measurements have produced extensive data on the time evolution of individual rotational states  $J'$  in HF( $v=2$ ) following laser excitation of molecules into a single state  $J$ . To extract individual rate constants we have previously used several scaling relationships in an iterative routine which fits the observed signal using level-to-level rate constants derived from scaling relations. (R. A. Copeland and F. F. Crim, J. Chem. Phys. 78, 5551 (1983)). These empirical scaling laws are based on the energy defect for rotational energy transfer. New work using relations based on the energy correct sudden approximation shows the deficiency of the energy based relations at high rotational levels and points to a multiple rotational quantum pathway ( $\Delta J \geq 2$ ) which contributes  $> 20\%$  to the total relaxation rate. This analysis permits detailed comparison with the results of linewidth analysis and shows that the two techniques seem to be sensitive to somewhat different aspects of the relaxation dynamics. Both measurements yield consistent values for the magnitude of the relaxation rate constants (R. A. Copeland and F. F. Crim, J. Chem. Phys. (in preparation)).

6. Publications:

R. A. Copeland and F. F. Crim, "Rotational Energy Transfer in HF(v=2): Experimental Measurements and Fitting Law Analysis", J. Chem. Phys. 78, 5551 (1983).

G. M. Jursich, D. R. Ritter, and F. F. Crim, "Vibrational Relaxation of HF(v=3,4,5) by H<sub>2</sub>, D<sub>2</sub>, CH<sub>4</sub>, CD<sub>4</sub>, and CO<sub>2</sub>", J. Chem. Phys. 79 (in press).

7. Extenuating circumstances:

none

8. No unspent funds will remain at the end of the contract period.

9. One graduate student will have received his degree during the contract period.

D. R. Ritter (M.S.)

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