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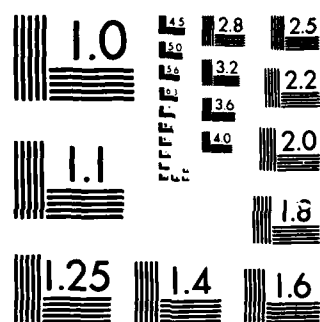
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The combination of laser excitation of overtone vibrations with time
resolved spectroscopic detection of reaction products provides uniquely
detailed data on the rates and disposal of energy into products in unimolecular
decompositions. The decomposition of a cyclic peroxide, tetramethyldioxetane,
is the first example of a vibrational overtone initiated reaction studied
in a free jet expansion, where the thermal energy content of the reacting
molecules is small. Low pressure gas phase data on hydrogen peroxide reveal

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the partitioning of the excess energy of the reaction in the OH products and provide new data on the vibrational overtone spectroscopy of this molecule. A new molecular beam apparatus has been constructed for extending these studies to a wider range of molecules using additional detection techniques.

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INTRODUCTION

The decomposition of a complex chemical system often contains a unimolecular reaction, in which an energized molecule rearranges or fragments, as a central step. Thus, complicated reactions can proceed through an initial elimination or molecular isomerization followed by extensive exothermic subsequent reactions. Our Army Research Office funded work is directed toward obtaining a detailed understanding of these crucial unimolecular initiation steps by experimentally studying the reaction dynamics of selectively energized molecules using direct excitation of overtone vibrations in combination with time and state resolved product detection.

A prime motivation for our studies is the need to combine a selective and well-characterized energy deposition scheme with direct observation of reaction rates and product quantum states in order to unravel the dynamics of both simple and complex molecular decompositions. Our experiments directly measure the unimolecular reaction rate constants for selectively energized molecules and hold the possibility of identifying the decomposition pathways in complicated molecules that might follow more than one reaction route. Directly measuring the reaction rate constant in a selectively energized molecule is important for testing and possibly extending theoretical descriptions of the reactions of energetic molecules. In particular, modeling of complex systems, on which direct measurements are impossible, employs statistical theories of unimolecular reactions. Detailed experiments on simpler reactions that still contain many important aspects of the more complex system serve to test the accuracy of theoretical methods. Decomposition of an energetic material is an example of a multistep process in which unimolecular production of a reactive fragment

initiates an involved series of subsequent reactions. These processes are very difficult to study in practical materials, but the essential features of the unimolecular reaction are present in simpler prototype compounds, most notably those containing weak N-O and N-N bonds.

The excitation specificity possible with direct excitation of overtone vibration also allows us to explore the role that the initially excited mode plays in determining the reaction rate and energy partitioning in a unimolecular decomposition. Energy partitioning among the reaction products is particularly relevant to the progress of complex decompositions because an energized fragment or isomer is often responsible for initiating further exothermic reactions. An important facility, which we have developed with ARO support, is a versatile new molecular beam apparatus incorporating mass spectrometric detection. This apparatus adds new scope to our work.

An informative time-resolved study of molecular decomposition requires a selective excitation technique that provides a known energy increment to the reaction products.¹ An even better excitation scheme would create the molecule with a known energy content, and the best possible situation would prepare the reactant in a single known quantum state. Vibrational overtone excitation offers these possibilities. Single photon excitation of an overtone vibration adds energy $h\nu$ to the initial thermal vibrational energy of the molecule, providing a known energy increment. An important limitation is the uncertainty introduced by transitions from

thermally populated vibrational states, which leave the molecules with a distribution of energies determined in part by the initial thermal energy distribution. In cases, usually small molecules, where detailed analysis of vibrational excitation spectra is possible, initial states can often be identified and the initial excitation known quite precisely. Our recent analysis of the overtone vibration spectra of $\text{HOOH}(5\nu_{\text{OH}}, 6\nu_{\text{OH}})$, which is discussed below, is an example.²

The most incisive comparison with theory comes from experiments in which the excited molecule has no initial thermal excitation. One major goal of our work has been to achieve such comparisons by studying the vibrational overtone induced decomposition of a molecule cooled in a pulsed supersonic expansion. Recent measurements on the decomposition of tetramethyldioxetane in a mild expansion demonstrate the feasibility of obtaining kinetic information by directly monitoring the time-evolution of the chemiluminescent product of the unimolecular decomposition.³ The potentially great spectroscopic resolution possible for many molecules under such conditions offers the opportunity for extremely specific initial excitation. Consequently, we have now constructed a molecular beam apparatus suitable for studying a variety of molecules using laser induced fluorescence or multiphoton ionization detection. We have established the techniques for performing time-resolved studies of molecular decomposition using vibrational overtone excitation coupled with chemiluminescence^{4,5} or laser induced fluorescence⁶⁻⁸ detection in low pressure bulk samples, and our new molecular beam data show that we can extend these techniques to molecules in supersonic expansions.

RECENT RESULTS

Our work on time-resolved unimolecular decompositions has been directed along three major lines. In low pressure bulk experiments, we have used laser induced fluorescence to study hydroperoxide decompositions⁶⁻⁸ and have learned about the unimolecular reaction rate, overtone vibration spectroscopy, and product energy partitioning in these molecules. In our recent molecular beam experiments, we have measured the decomposition rate of a molecule cooled in a supersonic expansion, in order to remove complications that arise from having a distribution of initial thermal vibrational energies. Finally, in a major construction effort, we have built a flexible new molecular beam apparatus for use in a number of the studies described in this proposal.

Low Pressure Bulk Measurements

Our earliest low pressure bulk measurements of overtone vibration initiated unimolecular decay used product chemiluminescence detection. During the past period of ARO support, we have extended the measurements to use laser induced fluorescence detection to obtain an extremely detailed view of the decomposition of hydrogen peroxide⁷⁻⁹ and t-butylhydroperoxide⁶ following selective excitation. Figure 1 shows our experimental apparatus.⁸ Running the experiment under the control of a laboratory computer facilitates the extensive signal averaging required in overtone vibration experiments. The computer controls the delay between the lasers and the wavelengths of both lasers, measures the powers of both lasers on every pulse, and accumulates the signal from the gated integrator. A Nd:YAG/dye laser provides excitation photons and a frequency doubled N₂ laser excited grazing incident dye laser provides ultraviolet probe light.

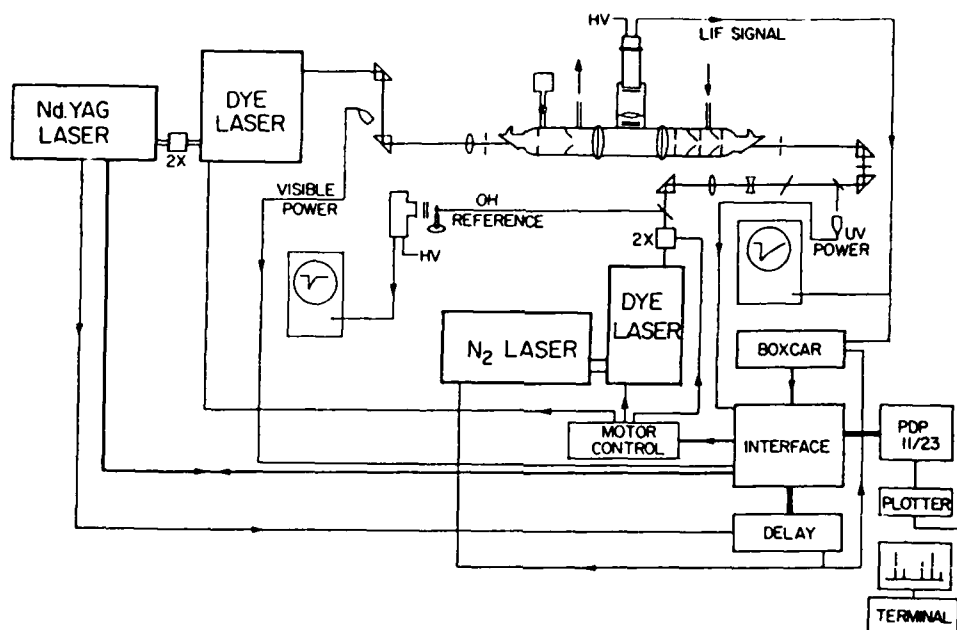


Figure 1

This apparatus has proven efficient and reliable in low signal level experiments on hydroperoxides.⁷⁻⁹

Our selective excitation studies on *t*-butylhydroperoxide (*t*-BuOOH) illustrate the ability of experiments using vibrational overtone preparation and time-resolved spectroscopic product detection to measure the unimolecular decay rate of a highly vibrationally excited molecule directly. A 6 ns pulse from the excitation laser excites the $5\nu_{OH}$ (46 kcal mol^{-1}) or $6\nu_{OH}$ (52 kcal mol^{-1}) vibration of *t*-BuOOH, and a 10 ns probe laser pulse interrogates a single rotational state of the OH fragment produced by breaking the 44 kcal mol^{-1} O-O bond. Varying the time delay between the lasers produces temporal evolution data, like those shown in Figure 2 for *t*-BuOOH($6\nu_{OH}$), from which we can extract the unimolecular decay rate of the selectively excited molecule. Detailed

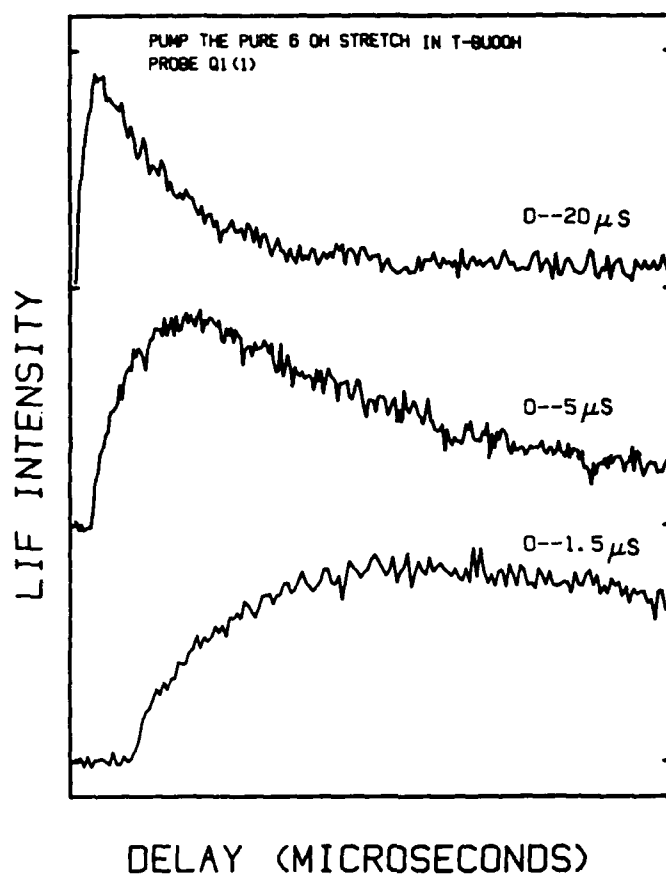


Figure 2

analysis requires proper consideration of rotational relaxation of the nascent OH fragment, particularly for the lower energy $5\nu_{\text{OH}}$ excitation but the data on t-BuOOH($6\nu_{\text{OH}}$) yield a decay rate constant, $k(E) \sim 4 \mu\text{s}^{-1}$, that is consistent with RRKM calculations.¹ This one example illustrates the power of the technique and points to a variety of similar experiments using LIF detection or MPI detection, depending on the product to be monitored.

The spectroscopic resolution available in both the excitation and detection provide even more detailed information on the dynamics of highly vibrationally excited molecules and on the partitioning of energy

in decomposition products. Our recent work on HOOH and HOOD is a particularly good example.⁷⁻⁹ Fixing the probe laser on the $Q_1(3)$ transition of the OH fragment from HOOH and varying the excitation laser wavelength in the region of the $6\nu_{OH}$ transition maps out the vibrational overtone excitation spectrum for those molecules that decompose into the observed state. (For HOOH, a dependence of the excitation spectrum on observed level becomes apparent only at high ($N \sim 10$) rotational states.) The excitation spectrum, shown in Figure 3, has two important features: There is clear, inhomogeneous rotational structure on the main vibrational overtone transition, denoted S_0^0 , and there are two additional features at higher energy, S_1^1 and S_0^1 . The most prominent rotational structure is the $^P Q_K$ branch, in symmetric top notation, with a characteristic doubling of levels caused by low lying torsional states.

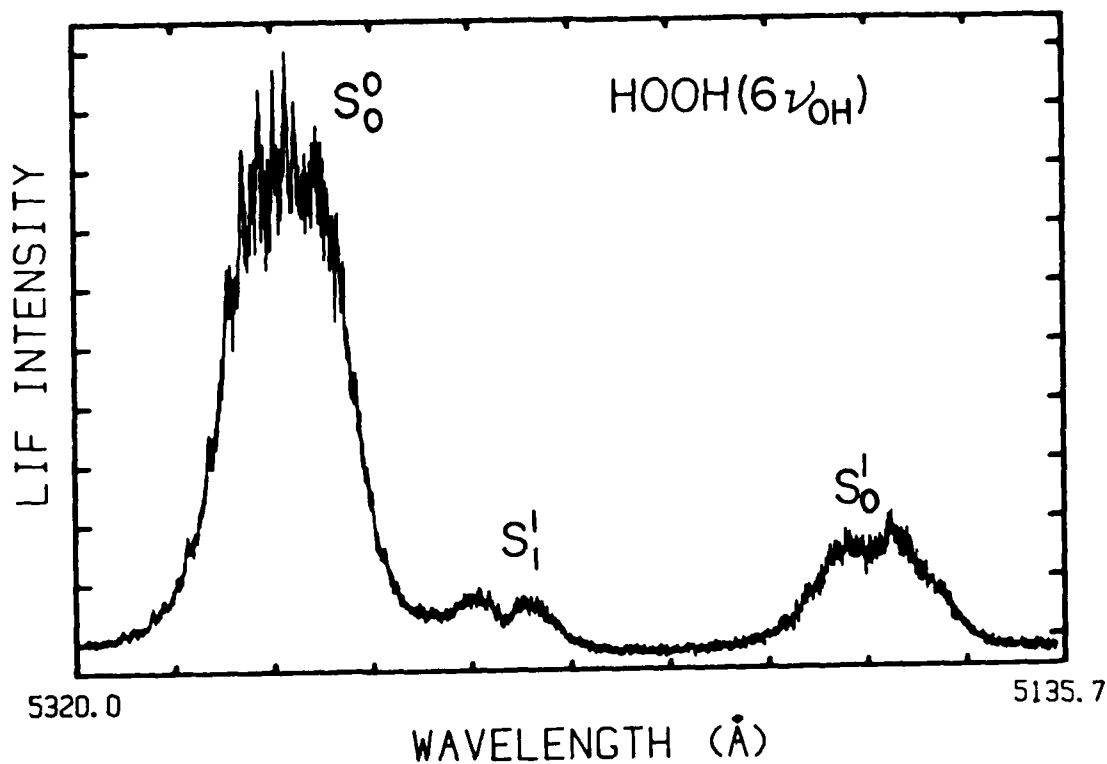


Figure 3

Calculations in our laboratory² have allowed us to unravel the coarse vibrational structure and to identify a Coriolis interaction that influences the rotational fine structure. Because thermal congestion obscures many of the features, a current goal is to measure the vibrational overtone excitation spectrum of HOOH cooled in a supersonic expansion.

We previously assigned the highest energy feature to a combination of $6\nu_{\text{OH}}$ with a torsion in HOOH^{7,8} and, now, have analyzed the intensities and positions of the transitions using a Born-Oppenheimer separation of the high frequency OH stretch and the low frequency torsion.² The highest frequency transition S_0^1 is indeed a combination involving the torsion in the vibrationally excited molecule. (S_0^1 refers to no torsional excitation in the lower state and one quantum in the upper vibrational state. The S refers to a torsional wavefunction that is symmetric with respect to the trans barrier to rotation of the OH groups around the O-O axis.) The other feature S_1^1 arises from a hot band in the lower state. Because these new spectroscopic insights provide a relatively complete description of the initially excited state, they are important in our analysis of the unimolecular reaction dynamics of highly vibrationally excited molecules.

Product state distributions reveal the energy partitioning in unimolecular reactions. Converting the laser induced fluorescence excitation spectra, obtained by fixing the vibrational overtone excitation wavelength and varying the probe laser wavelength, to individual state populations provides data for comparison to theoretical models. Figures 4 and 5 show the distributions resulting from excitation of the $6\nu_{\text{OH}}$ transition (S_0^0) and from excitation of the combination band $6\nu_{\text{OH}} + \nu_{\text{torsion}}$ (S_0^1). The solid curves are statistical (phase space) calculations that are constrained only to conserve total energy and angular momentum.⁸ The statistical theory does well for excitation of the pure overtone transition but is not so successful for the combination band. The failure

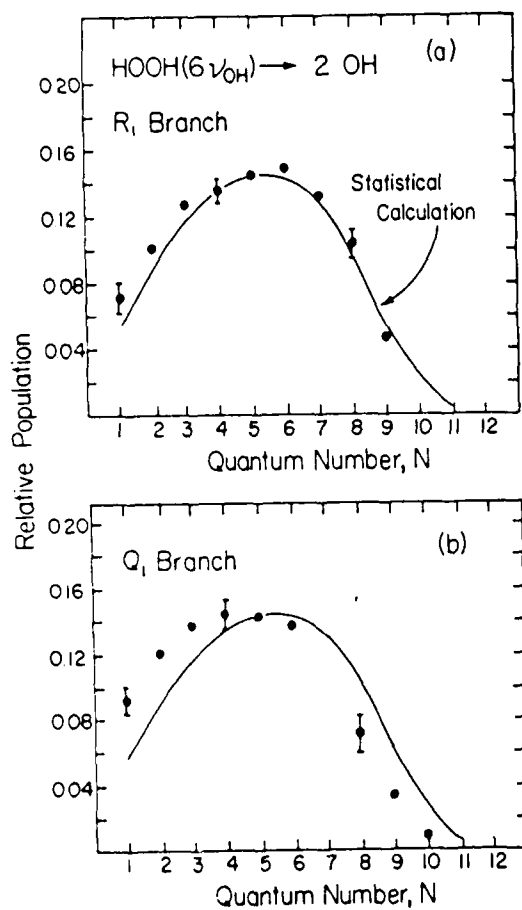


Figure 4

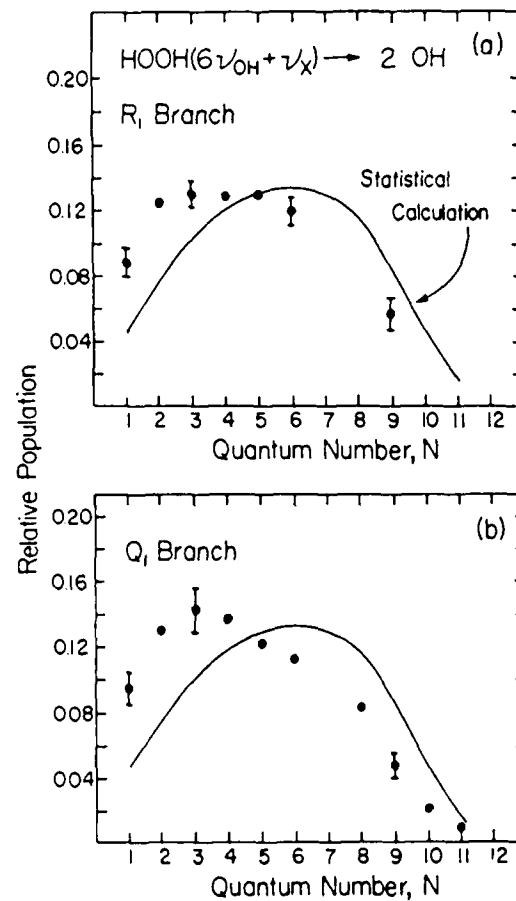


Figure 5

is not only quantitative. The distribution from combination band excitation shifts to lower energy, in qualitative disagreement with the predictions of statistical energy disposal.⁸ This may reflect selective coupling of the initially excited torsion to the rest of the molecule on the time-scale of the decomposition.

A final interesting result that points to the wealth of detail possible in vibrational overtone initiated decompositions comes from exciting the fourth overtone vibration ($5\nu_{\text{OH}}$) in HOOH .⁹ Although the added energy is less than the strength of the O-O bond, molecules initially containing more than about 1100 cm^{-1} of vibrational-rotational energy can dissociate. This drastically changes the vibrational overtone excitation spectrum that we observe by monitoring the OH product. As Figure 6(a) shows, the spectrum has a great deal more structure than that obtained in the $6\nu_{\text{OH}}$ region. Also, the spectra change drastically with the identity of the probed rotational level. The spectrum in Figure 6(b), obtained probing $N=7$, differs drastically from that observed probing $N=1$ (Figure 6(a)). These data provide a test for the model of torsional structure in $6\nu_{\text{OH}}$.² We find that the model nicely explains the general features of the $5\nu_{\text{OH}}$ spectra. Finally, we are analyzing these $5\nu_{\text{OH}}$ spectra to understand the torsional, vibrational, and rotational hot band structure in the molecule better. (For example, comparing $6\nu_{\text{OH}}$ to $5\nu_{\text{OH}}$ proves that the additional features involve torsions and not Fermi resonant bends.²)

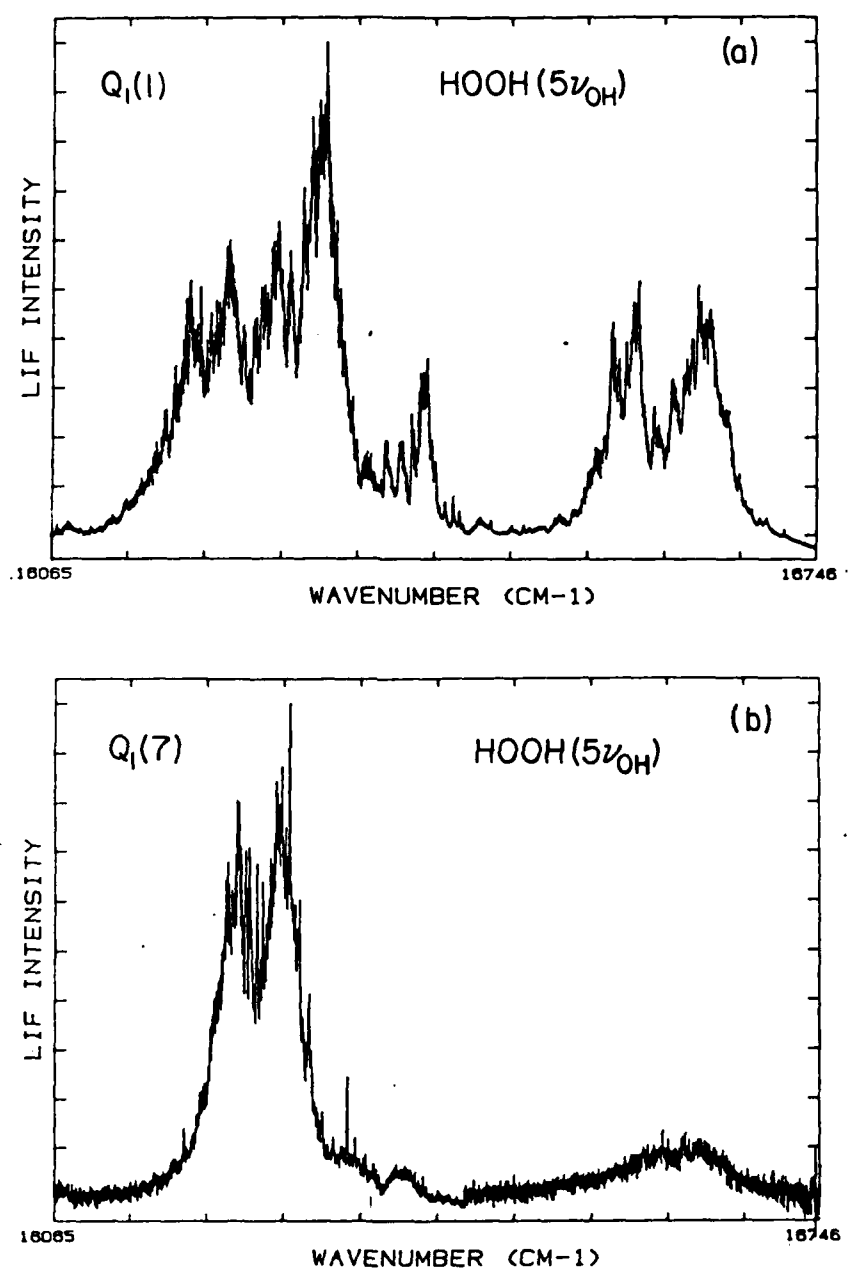


Figure 6

Molecular Beam Measurements

A major goal of our time-resolved studies of molecular decomposition has been to measure the unimolecular decay rate of a selectively energized molecule without the complication of initial thermal vibrational energy. Such data, which provide an incisive comparison with theory, are obtainable for reactions carried out in the cold environment of a supersonic expansion. Recent measurements on the unimolecular decomposition of tetramethyldioxetane in a molecular beam demonstrate the feasibility and usefulness of these experiments.

Tetramethyldioxetane (TMD) is a cyclic peroxide that decomposes over a barrier of about 26 kcal mol^{-1} to produce, in part, electronically excited acetone. In earlier low pressure bulk experiments⁴, we directly measured the unimolecular decay rate of highly excited TMD ($4\nu_{\text{CH}}$ or $5\nu_{\text{CH}}$) by monitoring the time-evolution of the product emission following pulsed vibrational overtone excitation. Now, by seeding TMD into a molecular beam, we have succeeded in measuring the decomposition rate of TMD($4\nu_{\text{CH}}$) cooled in a supersonic expansion. The apparatus is a single vacuum chamber containing a pulsed molecular beam source and a photomultiplier tube for observing product chemiluminescence. (Because TMD decomposes on contact with metal surfaces, the nozzle is almost entirely glass, a technology that will be useful for handling other sensitive compounds.) The 905 nm light from a Nd:YAG/dye laser intersects the 300 μs molecular beam pulse at right angles, and the product emission perpendicular to the two enters the photomultiplier. This apparatus is also excellent for obtaining low pressure bulk data, with the principle improvement over our previous experiments⁴ being the ability to use near-infrared dyes to generate excitation light without Raman shifting.

Observing total product emission as a function of excitation wavelength provides vibrational overtone spectra for TMD. Comparing the spectrum of a low pressure bulk sample (~ 2 mTorr) with that obtained in a mild (60 Torr) He expansion reveals definite differences arising from changes of hot band populations. These data are a means of assessing the magnitude of the homogeneous and inhomogeneous structure in the vibrational overtone spectra.

The most dramatic example of the cooling in the expansion comes from observing the time-evolution of the chemiluminescent product. This is, of course, the primary goal in our time-resolved molecular decomposition studies because it provides the unaveraged data needed for detailed comparison with theory. We previously compared our time-evolution data to RRKM calculations by averaging over a distribution $P(\epsilon)$ of thermal vibrational energy to obtain a calculated time evolution, $\int P(\epsilon) \exp[-k(\epsilon + h\nu)t] d\epsilon$, where $k(E = \epsilon + h\nu)$ is the theoretical (RRKM) rate constant as a function of total energy and $h\nu$ is the photon energy. This approach nicely recovers the detailed time-evolution of the observed signal.⁴ (Simply evaluating the rate constant at the average thermal vibrational energy does not produce the correct time-evolution.) Cooling the molecule in a supersonic expansion greatly reduces the thermal vibrational energy content so that, ideally, $P(\epsilon)$ becomes a δ -function. Completely removing the internal energy of a molecule the size of TMD is unlikely, particularly for our modest expansions. (Higher pressure expansions seem to produce unacceptable clustering of the molecules.) However, substantially lowering the thermal energy content produces a noticeable change in the decomposition kinetics. Figure 7(a) shows the time-evolution of a 2.2 mTorr sample of TMD, and Figure 7(b) shows it for a 60 Torr He expansion containing $\sim 0.5\%$ TMD. (The data come from averaging 10 000 and 30 000 laser shots, respectively.) The obviously slower rise in the latter data reflects the reduced thermal energy content. These

are just the type of data we can compare directly to theory with much reduced thermal averaging. In order to assess the energy content of the molecules independently, we have obtained and analyzed the laser induced fluorescence spectra of biacetyl under similar expansions conditions. These data clearly demonstrate the feasibility of studying other molecules cooled in molecular beam.

New Molecular Beam Apparatus

A major construction effort during the past period of ARO support has been directed toward a molecular beam apparatus that provides extensive new capabilities that add considerable scope to our time-resolved studies of molecular decomposition. The advantages of cooling molecules have been described in connection with our recent molecular beam measurements, and, although our new apparatus has very good capabilities in this regard, the primary motivation for building it is to exploit multiphoton ionization detection fully. This is a differentially pumped apparatus that allows us to produce intense pulsed or continuous molecular beams and to detect them by laser induced fluorescence, multiphoton ionization time-of-flight mass spectrometry, or electron impact time-of-flight mass spectrometry.

Figure 8 is a schematic drawing of the principle features of the apparatus. The molecular beam, generated in a separately pumped source, passes through one or more skimmers and a differentially pumped buffer region into the interaction zone where it is crossed by excitation and probe laser beams. For multiphoton

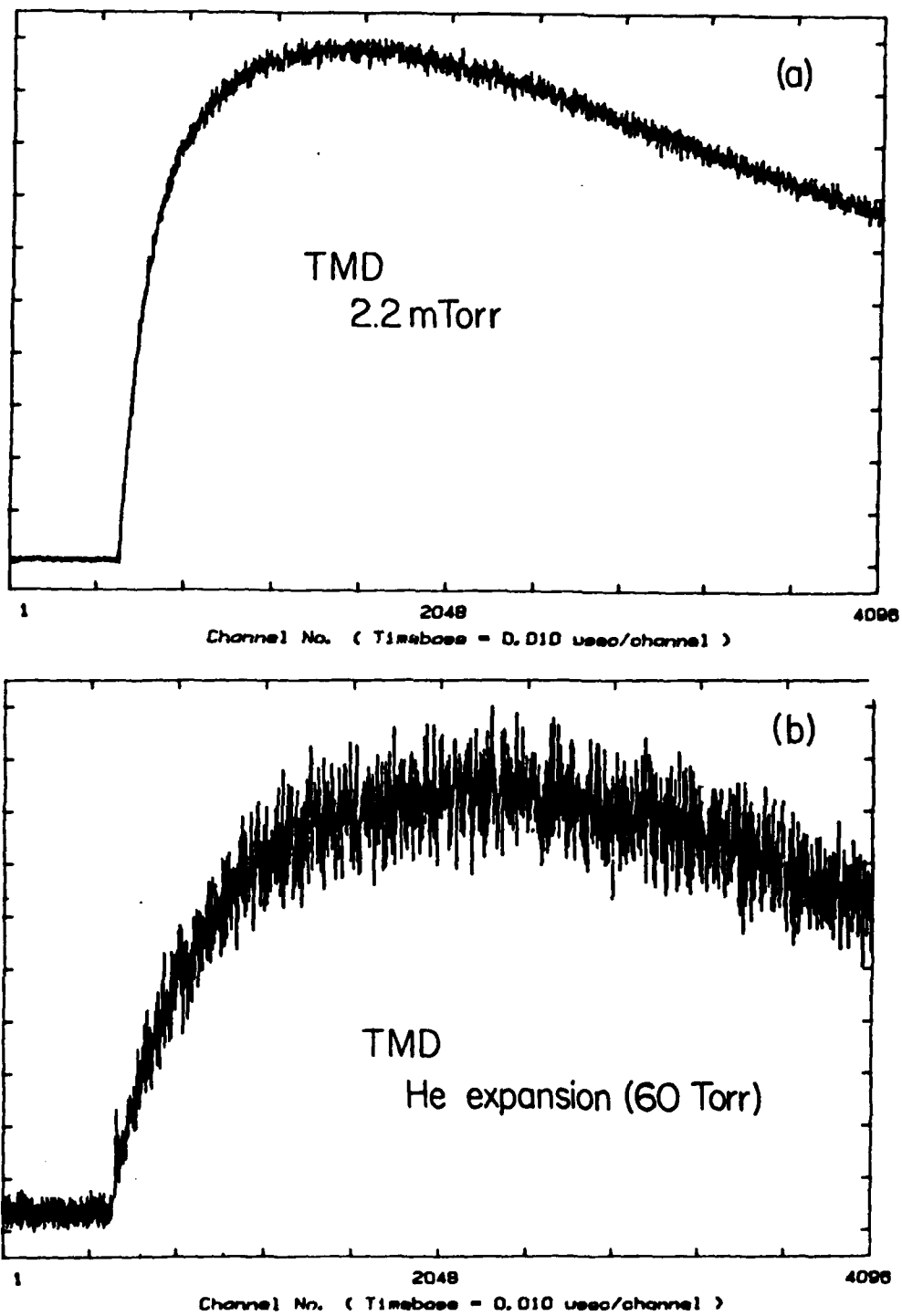


Figure 7

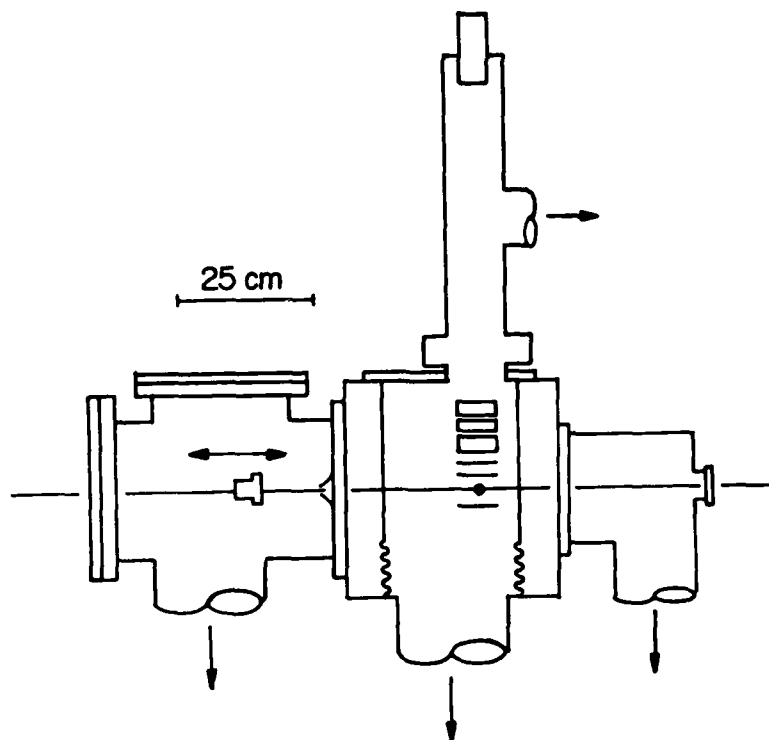


Figure 8

ionization detection, the ions are created in the accelerating region of a Wiley-McLaren design time-of-flight mass spectrometer. Several laser ports provide a number of excitation locations, and there are two ionizer positions to allow detection very close to the beam source if desired. The large ionizer is designed to use the high spatial and temporal resolution of MPI detection to obtain recoil speed and angle distributions for the fragments. Focussing the ionizing laser a fixed distance from the vibrational overtone excitation laser and varying the delay between the two provides the fragment speeds by an optical time-of-flight measurement. Varying the angular location measures the recoil direction of the fragments.

There are a variety of configurations for the apparatus in addition to the one shown, and a large number molecular beam-multiple laser experiments, such as exciting along the beam or well before the ionizer, are possible. Because the TOF mass spectrometer has an electron bombardment ionizer, it meets a much broader range of needs than MPI detection alone. For example, we intend to use it for beam diagnostics and perhaps for detection of vibrationally excited molecules by low energy electron bombardment ionization. The mass analysis capability also gives us the possibility of distinguishing isomers by fragmentation pattern differences even if they have similar transitions in MPI. The most important feature of this apparatus is its flexibility, which allows us to attempt many different time and state resolved experiments.

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BIBLIOGRAPHY

1. F. F. Crim, Ann. Rev. Phys. Chem. 35, 657 (1984).
2. H-R. Dübal and F. F. Crim, J. Chem. Phys. 83, 3863 (1985).
3. E. S. McGinley and F. F. Crim, J. Chem. Phys. 84, 1986 (in press).
4. B. D. Cannon and F. F. Crim, J. Chem. Phys. 75, 1752 (1981).
5. B. D. Cannon and F. F. Crim, JACS 103, 6722 (1981).
6. T. R. Rizzo and F. F. Crim, J. Chem. Phys. 76, 2754 (1982).
7. T. R. Rizzo, C. C. Hayden, and F. F. Crim, Faraday Discuss. Chem. Soc., 75, 223 (1983).
8. T. R. Rizzo, C. C. Hayden, and F. F. Crim, J. Chem. Phys. 81, 4501 (1984).
9. T. M. Ticich, T. R. Rizzo, H-R. Dübal and F. F. Crim, J. Chem. Phys. 84 (in press).

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