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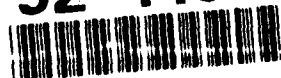
THE PATHWAYS AND DYNAMICS OF MOLECULAR DECOMPOSITION

DAAL03-88-K-0189

CONTENTS

TABLE OF CONTENTS	i
ABSTRACT	ii
INTRODUCTION	1
TECHNIQUES AND RESULTS	3
Vibrational Overtone Induced Dissociation	4
Vibrationally Mediated Photodissociation	8
Energy Selective Ionization	12
REFERENCES	19
PERSONNEL SUPPORTED	22
PUBLICATIONS	22

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ABSTRACT

Molecular decompositions often control complex chemical reactions by producing a highly reactive fragment that determines the subsequent chemistry. Despite the importance of such processes, there is little detailed information available for testing theoretical models and guiding the analysis of practical systems. This report describes experiments that produce, characterize, and dissociate highly energized molecules in order to uncover the details of molecular decomposition. These experiments create highly energized molecules either by vibrational overtone excitation or electronic excitation and detect the products either by a state-resolved laser detection technique, such as laser induced fluorescence, or by energy-selective ionization using vacuum ultraviolet photons. The state-resolved measurements probe the decomposition dynamics by determining the quantum state populations in the products and their appearance rates. These data provide a particularly good point of comparison with theoretical models and are a test of the applicability of statistical theories. The energy-selective ionization studies can also provide rate information but are most valuable as a means of identifying the primary dissociation products and their recoil energies. The use of vacuum ultraviolet photons makes our apparatus very sensitive. We have proven the technique on electronic photodissociation of a series of nitroalkanes and on nitrobenzene.

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INTRODUCTION

The crucial step in a complex chemical reaction is often the fragmentation of a molecule to produce energetic and reactive products that control the subsequent chemistry. For example, the production of a reactive fragment might be the first step in a complicated sequence of exothermic reactions. Our Army Research Office sponsored work studies these fundamental events in energized molecules by selective excitation in combination with time- and state-resolved interrogation of excited molecules and reaction products. A central motivation for our work is the need to combine a selective and well-characterized energy deposition scheme with direct observation of reaction products, their formation rates, and their quantum state populations in order to unravel the dynamics of both simple and complex molecular decompositions. Our experiments directly observe unimolecular reactions in selectively energized molecules and identify decomposition pathways in complicated molecules. These detailed studies are the means of critically testing and extending theoretical descriptions of molecular dissociation. In particular, modelling complex systems, on which direct measurements are impossible, employs statistical theories and includes assumptions about decomposition pathways. Experiments on simpler reactions that contain many important aspects of the more complex system serve to test and validate the theoretical models. The decomposition of an energetic material is an example of a complex, multistep process in which a molecular dissociation initiates an involved series of subsequent reactions. Detailed studies of prototypical compounds, particularly those containing weak N-O and N-N bonds, can reveal the essential details of the decomposition. The goal of our Army Research Office supported program is the study of molecular decomposition by the production, characterization, and dissociation of highly energized species in both their ground and

electronically excited states. We employ several approaches and have studied the unimolecular decomposition of highly vibrationally excited molecules, the electronic photodissociation of highly vibrationally excited molecules, and the decomposition of electronically excited molecules.

We use vibrational overtone excitation to prepare highly vibrationally excited molecules selectively, and we have exploited it extensively in studying molecular decompositions.^{1,2,3} The one-photon excitation of a vibrational overtone transition, which derives its oscillator strength from a stretching vibration involving a light atom, deposits a known energy increment in the molecule in a manner that is quite different from thermal excitation. Because characterization of the initially excited state is one of the important aspects of studying the dynamics of such highly energized molecules, we have developed new techniques that use laser induced fluorescence,⁴ photodissociation,^{5,6} or ionization⁷ to probe the excited molecules. Taking full advantage of the selectivity of the excitation requires that we monitor the appearance of reaction products and determine the partitioning of the products among their quantum states. The former observation provides rate information and the latter measures the energy disposal in the fragments. Energy partitioning among the reaction products is particularly relevant to the progress of complex decompositions because an energized fragment is often responsible for initiating further reactions. We have continued to use time-resolved laser induced fluorescence^{8,9} to monitor products and have also developed a new approach, which we have initially applied to electronic photodissociation, that uses energy-selective vacuum ultraviolet photoionization.^{10,11,12}

A fundamental question about molecular decompositions, particularly complex dissociations, is simply the identity of the primary products. Again, this is a particularly important question in complicated systems where the initial product may control the

subsequent chemistry. We have demonstrated that the versatile molecular beam apparatus¹¹ we constructed with Army Research Office support can provide the answers to such questions.^{10,12,13,14} Our detailed studies have employed several approaches to probe different aspects of molecular decomposition and have opened several new possibilities. We have combined laser excitation of overtone vibrations with time- and state-resolved detection for detailed studies of unimolecular decomposition in both room temperature samples^{1,2,8,9} and in supersonic expansions.^{2,15,16} These experiments have determined the nature of the initially excited state, the rate of unimolecular decomposition, and the partitioning of energy among the states of the reaction products. In addition, we have demonstrated electronic photodissociation techniques that allow us to characterize highly vibrationally excited molecules, to produce unique dynamics in the electronic photodissociation of vibrationally excited molecules,^{5,6} and to identify the primary fragments of molecular photodissociations, even at the level of measuring the kinetic energy release.^{10,12,13,14}

TECHNIQUES AND RECENT RESULTS

Our recent Army Research Office supported work produces, characterizes, and dissociates highly energized molecules. Our production of highly vibrationally excited molecules uses one-photon excitation of overtone vibrations, and we have employed this excitation for **vibrational overtone induced dissociation** in several molecules in both room-temperature gases and in cold supersonic expansions as a means of determining unimolecular reaction rates and product energy partitioning. We have also developed the technique of **vibrationally mediated photodissociation**, in which we electronically photodissociate a highly vibrationally excited molecule, both as a means of characterizing initially

prepared vibrational states and of producing unique electronic photodissociation dynamics. In a somewhat different approach, we have implemented an **energy-selective ionization** scheme for identifying the primary products of a dissociation and measuring their kinetic energy. This section reports our work in each of these three areas and describes the approaches we have developed for the new experiments that we propose.

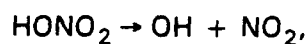
Vibrational Overtone Induced Dissociation

We have studied the vibrational overtone induced dissociation of several molecules ranging from the small tetra-atomic and penta-atomic molecules HOOH ⁸ and HONO_2 ⁹ to very large species such as tetramethyldioxetane,¹⁶ which contains 20 atoms. In these experiments, we prepare a highly vibrationally excited molecule by laser excitation of an overtone vibration and then interrogate the products spectroscopically using either product chemiluminescence^{16,17} or laser induced fluorescence.^{8,9} The latter technique determines the population of individual product quantum states as well as providing rate information.

We have taken two approaches to determining the unimolecular reaction rates of molecules with excited overtone vibrations. One is quite direct in that we spectroscopically monitor the appearance of reaction products as a function of time. Because the 10-ns duration of our laser pulses determines the time resolution of this method, we apply it to large molecules whose unimolecular reaction rates are slow enough to resolve.¹⁶ Our second approach is a more inferential scheme in which we attempt to observe single, homogeneous lines in a vibrational overtone spectrum and determine the unimolecular reaction rate from the widths of these features.¹⁵ This technique is complementary to the first since it is best applied to small molecules that react so rapidly that the resulting linewidth substantially

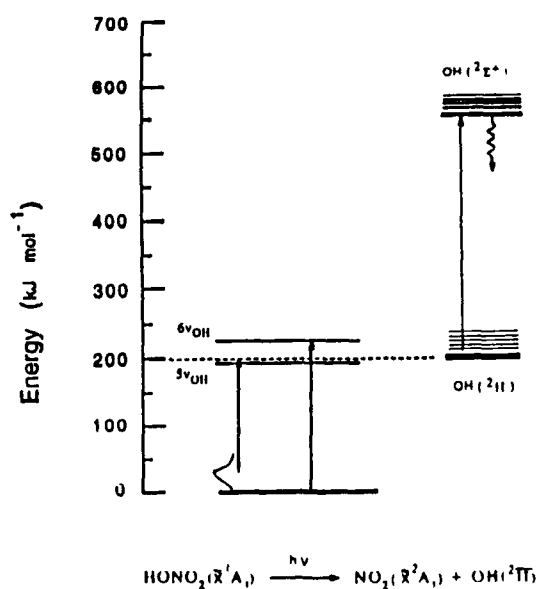
exceeds our limiting laser resolution of about 0.05 cm^{-1} . Performing both experiments on molecules cooled in a free jet expansion is an important aspect of our approach since it reduces the distribution of initial thermal energies in large molecules¹⁷ and provides the spectral simplification required to observe isolated features in small molecules.¹⁵

Our most detailed unimolecular decomposition studies have used the diagnostic of the distributions of the products among their quantum states to test models of the decomposition dynamics.^{8,9} The population distribution is potentially a sensitive probe of the decomposition dynamics, as shown by our measurements and their comparison to theory.¹⁸ Our study of the vibrational overtone induced decomposition of nitric acid,⁹



following excitation in the regions of the $5\nu_{\text{OH}}$ and $6\nu_{\text{OH}}$ transitions illustrates the utility of measuring product state distributions as a means of understanding the dynamics and comparing to theory. In these experiments, whose energetics Figure 1 shows, a pulsed dye

Figure 1



laser prepares a highly energized molecule by excitation in the region of either the fourth ($5\nu_{\text{OH}}$) or fifth ($6\nu_{\text{OH}}$) overtone of the O-H stretching vibration. The former excitation produces molecules very near to the decomposition barrier, which they are able to surmount with a small amount of additional thermal energy, and the latter excitation creates molecules with about 32 kJ/mol of energy in excess of the threshold. A second pulsed dye laser interrogates individual quantum states of the OH fragments from the reaction by laser induced fluorescence (LIF) and allows us to determine the relative populations of the vibrational, rotational, lambda-doublet, and spin-orbit states. These distributions are the key for the comparison to statistical models of the decomposition.

Figures 2 and 3 show the distributions of the OH products among their rotational states (solid bars) along with the predictions of phase space theory (PST) (open bars) for initial excitation of $5\nu_{\text{OH}}$ and $6\nu_{\text{OH}}$, respectively. Decomposition of $\text{HONO}_2(5\nu_{\text{OH}})$ forms OH with much less rotational excitation than the decomposition of $\text{HONO}_2(6\nu_{\text{OH}})$ since the excess energy is considerably smaller in the first case. The phase space theory calculations and the measurements agree quite well for the OH fragment populations in *both* spin-orbit states ($^2\Pi_{3/2}$ and $^2\Pi_{1/2}$) in the $5\nu_{\text{OH}}$ initiated decomposition (Figure 2). Phase space theory predicts not only the distribution of products among the rotational states within each spin-orbit state but also correctly predicts the relative amount of each produced. This prediction comes entirely from the conventional form of PST in which the population of all states that conserve energy and angular momentum (without regard to the electronic fine structure) is equally likely. The agreement between the measured OH rotational state distribution and the PST prediction for the decomposition of $\text{HONO}_2(6\nu_{\text{OH}})$ is qualitatively satisfactory but differs in detail. The theory predicts slightly more rotational energy in the product than we observe experimentally, and the PST theory prediction of almost comparable amounts in the two spin-

orbit states disagrees substantially with our observation of a 60% excess in the $^2\Pi_{3/2}$ state. The reduced rotational excitation in the OH products from $\text{HONO}_2(6\nu_{\text{OH}})$ compared to PST is consistent with the transition state becoming tighter at the higher energy excess energy.¹⁹

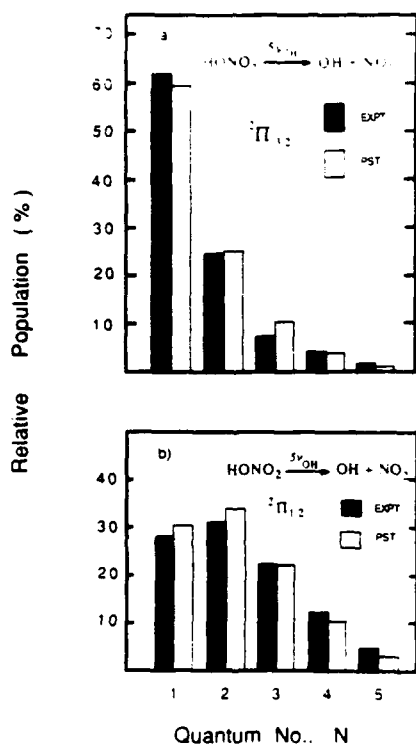


Figure 2

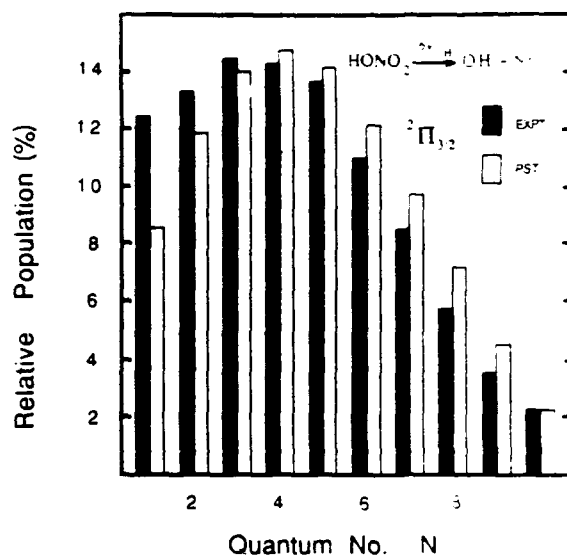


Figure 3

The consequent increase in the frequency of the bending vibrations, which correlate with rotations of the separated products, leads to less bending excitation in the transition state and, hence, less rotation in the products.

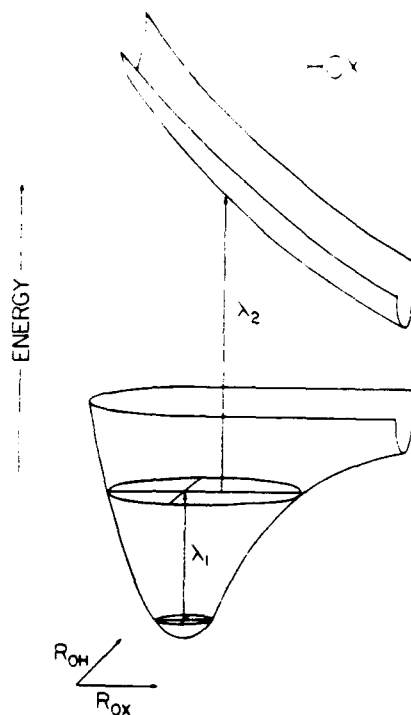
Vibrationally Mediated Photodissociation

The schematic drawing of a ground state potential energy surface and a repulsive electronically excited surface shown in Figure 4 describes vibrationally mediated photodissociation for an HOX molecule. (In our applications to date, X is H,²⁰ OH,⁵ NO₂^{2,6}, and t-BuO.⁵) This diagram shows the surfaces along the bond stretching coordinate (the O-H stretching vibration) and the dissociative coordinate (the O-X stretching vibration). The O-H vibration is bound in both the ground and electronically excited states, but the O-X vibration is unbound in the latter. Conventional photodissociation excites a molecule from a region near the minimum on the lower surface to the repulsive upper surface, but the two-step vibrationally mediated photodissociation process first excites a high vibrational level of the ground electronic state and, subsequently, dissociates the vibrationally excited molecule with a second photon. Thus, the dissociation occurs from a rather different part of the ground state potential energy surface than does the usual one-photon process. The energies of the excitation photon (λ_1) and dissociation photon (λ_2) shown in Figure 4 are each insufficient to dissociate the molecule from its equilibrium geometry, and the dissociation by the second photon must occur from a region in which the bond extension along the O-X coordinate brings the ground and excited electronic surfaces closer than in the equilibrium configuration. Vibrationally mediated photodissociation allows us to assess the nature of the state prepared by vibrational overtone excitation and to observe differences in the electronic dissociation dynamics of vibrationally excited molecules. Both types of information come from the participation of usually inaccessible parts of the ground and electronically excited potential energy surfaces in the vibrationally mediated photodissociation.

Varying the wavelength (λ_1) of the vibrational overtone excitation laser while

monitoring the products of the subsequent decomposition provides the absorption spectrum of those molecules that absorb another photon and dissociate to form products in the probed

Figure 4



quantum state. These vibrational overtone excitation spectra are a window on the state that we prepare in the highly vibrationally excited molecules. An extension of the local mode model using a zero-order state, which carries the oscillator strength for the transition, coupled to background states²¹ provides an extremely useful connection between spectral observations and couplings within a molecule. A central goal of our vibrational overtone spectroscopy is obtaining a description of the initially excited state as an admixture of zero-order states about which one has good chemical intuition. This is possible using vibrationally mediated photodissociation because the intensities of the transitions reflect the degree to which motion along the dissociation coordinate (O-X) is coupled with the local mode vibration corresponding to the zero-order state carrying the transition strength (O-H stretching). Because only those initial states that have a significant amount of O-X stretching

character can absorb the dissociation photon for the energetic situation illustrated in Figure 4, the production of fragments signals the participation of the zero-order O-X stretching state. We have used this approach to obtain vibrational overtone spectra of molecules in room temperature samples^{5,6} and in free jet expansions,^{3,15} and Sibert and coworkers have used these data as a test of theoretical models of the state mixing in hydrogen peroxide.²²

We measure the distribution of the OH products of vibrationally mediated photodissociation among their quantum states by laser induced fluorescence and determine the product recoil energy from the Doppler widths of the probe transitions. For hydrogen peroxide, this allows us to assess the energy disposal completely, and we can infer the internal energy of the other fragment for nitric acid ($X = \text{NO}_2$) and t-butylhydroperoxide ($X = \text{t-BuO}$). The larger NO_2 and t-BuO fragments from nitric acid and t-butylhydroperoxide acquire a considerably greater fraction (78% and 89%, respectively) of the available energy as internal excitation than do the OH fragments from hydrogen peroxide, which obtain only 29% of the total. The large amount of average internal energy ($19\,500\text{ cm}^{-1}$) in the NO_2 fragment suggests excitation of its low lying electronic states, and indeed we observe emission from the electronically excited fragment.⁶ The production of vibrationally excited fragments in the vibrationally mediated decomposition of HOOH and HONO_2 reflects a striking change in the dissociation dynamics compared to the case of one-photon ultraviolet dissociation. Ultraviolet dissociation of hydrogen peroxide at $\lambda = 355\text{ nm}$,⁵ 266 nm ,²³ 248 nm ,²⁴ and even 193 nm ²⁵ produces *no* vibrationally excited OH fragments compared to 10% to 20% for the vibrationally mediated process, depending on the energy of the dissociating photon (λ_2).⁵ The enhanced product excitation is not an energetic effect, since the ultraviolet excitation adds a larger amount of energy, but rather arises from the vibrational excitation influencing the dynamics of the dissociation.

Nitric acid behaves similarly in that vibrationally mediated photodissociation produces about 5% vibrationally excited OH fragments⁶ compared to none in the case of 280-nm one-photon dissociation.²⁶ We have sharpened this comparison even more by measuring the OH product state distribution for the decomposition of HONO_2 initiated by one-photon excitation with 241-nm light. This excitation adds the same energy as the two-photon vibrationally mediated photodissociation with $\lambda_1 = 755$ nm and $\lambda_2 = 355$ nm, but leads to rather different disposal of the energy. Figure 5 shows that the rotational distributions for the one-photon and the two-photon dissociations are essentially identical, but we find about three times more vibrationally excited OH from the vibrationally mediated photodissociation than

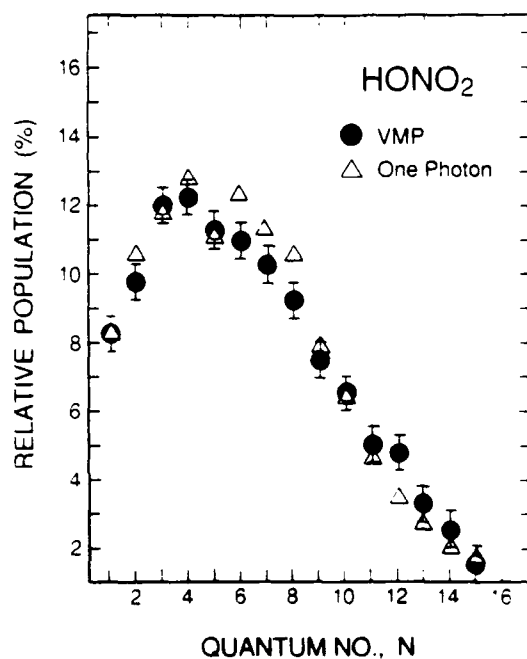


Figure 5

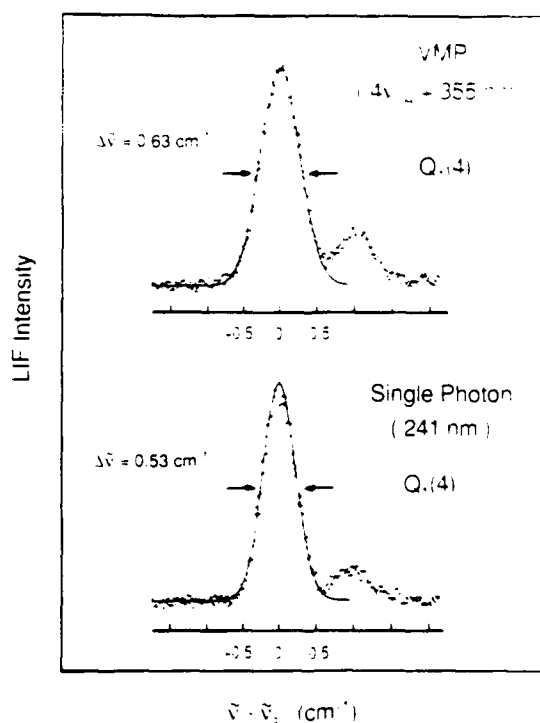


Figure 6

from the direct dissociation, although the fraction of vibrationally excited molecules is small

in both cases (6% versus 2%). The translational energy release is very different for the two processes. Figure 6 shows the Doppler profiles in the LIF excitation spectra of the OH products from the two dissociations. Even with the convolution with the laser linewidth, it is clear that vibrationally mediated photodissociation releases more energy into translation. After deconvoluting the laser linewidth, we find almost twice as much translational energy release in vibrationally mediated photodissociation (14% of that available) compared to single photon dissociation (7.5% of that available). Our observation of emission confirms that much of the considerable internal energy in NO_2 is electronic excitation. These measurements have allowed us to form a detailed picture of the single photon and vibrationally mediated photodissociation at several wavelengths based on the identity of the accessible electronic states in nitric acid, their correlation to the states of the products, and the influence that vibrational excitation on the ground electronic state potential has on the electronic transitions to those states.⁶

Energy Selective Ionization

We have recently demonstrated a scheme in which we use energy selective ionization to identify the primary products of an electronic photodissociation and to measure the kinetic energy released into the fragments^{10,11} This section briefly describes the approach in general along with its application to the dissociation of methyl iodide (CH_3I),¹⁰ nitromethane (CH_3NO_2),¹² nitroethane ($\text{C}_2\text{H}_5\text{NO}_2$),¹³ and nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$).¹⁴ We have used energy selective ionization to study the dissociation of CH_3I to prove our technique¹⁰ and have begun a systematic study of the decomposition dynamics of nitro compounds, RNO_2 , that is allowing

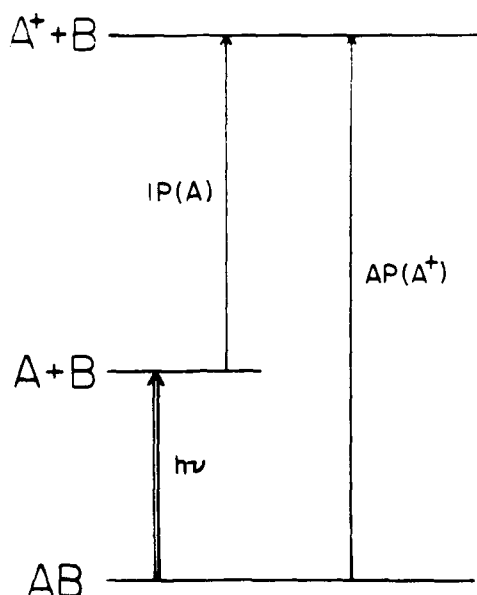
us to develop a consistent and detailed picture of their decomposition dynamics and pathways.^{12,13,14}

The key to these new experiments is a time-of-flight photofragment spectrometer that uses vacuum ultraviolet photons to ionize decomposition fragments selectively. The combination of energy selectivity and mass resolution in this approach makes it a direct and efficient means of identifying the primary fragments, and, hence, dissociation pathways, in molecular decompositions. The apparatus consists of a separately pumped source that produces a skimmed, pulsed molecular beam that enters a differentially pumped time-of-flight mass spectrometer. The heart of the energy selective ionization experiments is a mercury heat pipe in which we produce 9-eV (125-nm) photons by four-wave mixing of ultraviolet and visible light.²⁷ Our first experiments used low-energy electrons that we still find to be a helpful diagnostic in the apparatus, but the crucial advance, and one of our primary goals during this past funding period, has been the development of vuv photoionization capability. The development of this source has vastly increased the sensitivity of the apparatus and the potential scope of the measurements.

Figure 7 shows the energetics of using energy selective photoionization to detect photodissociation products. Using vacuum ultraviolet photons with energy between the ionization potential of the fragment we wish to probe [$IP(A)$] and the appearance potential of the fragment the precursor molecule [$AP(A)$] ensures that any signal at the mass of A^+ comes only from the photofragment. Because the ion detection is mass selective, this is a means of identifying the primary photofragments using a general detection scheme. The energetic discrimination shown in Figure 7 applies to all systems in which the appearance potential of a fragment exceeds the ionization potential of that fragment from the precursor molecule, a situation that obtains except for unusual cases where extensive fragment rearrangement

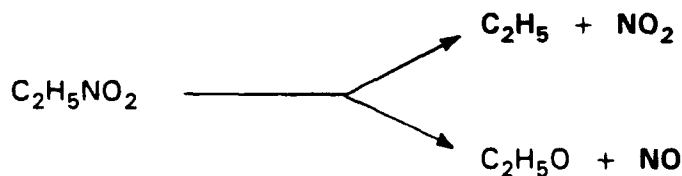
makes the dissociation very exothermic. Because vuv photoionization is a broadly applicable detection technique, we can study dissociation processes that produce fragments that are impossible to detect by resonant laser ionization or laser induced fluorescence. Our current apparatus uses a single dye laser to produce both the visible and ultraviolet photons that we

Figure 7



mix in Hg, and our primary equipment request, discussed below, is for the hardware to generate independent visible and ultraviolet photons in order to produce vuv photons of variable energy.

The time-of-flight mass spectrum in Figure 8 demonstrates vuv photoionization detection of the products of the 280-nm photolysis of nitroethane.¹³ We directly observe two decomposition channels,



since we monitor three of the four primary fragments (denoted as bold above) directly. The ethoxy ion is quite unstable, and the vinyl fragment (C_2H_3) that we observe probably comes from its decomposition. A number of detailed tests, including photolysis of ethyl iodide for

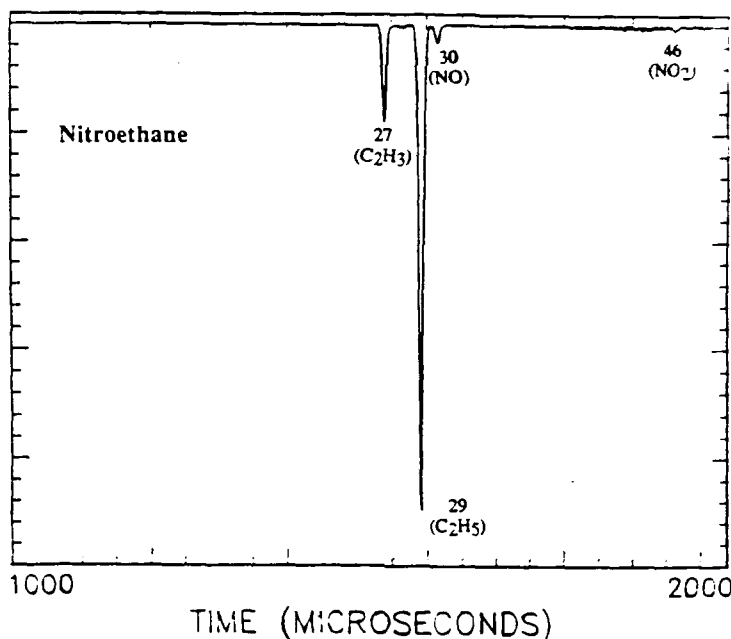
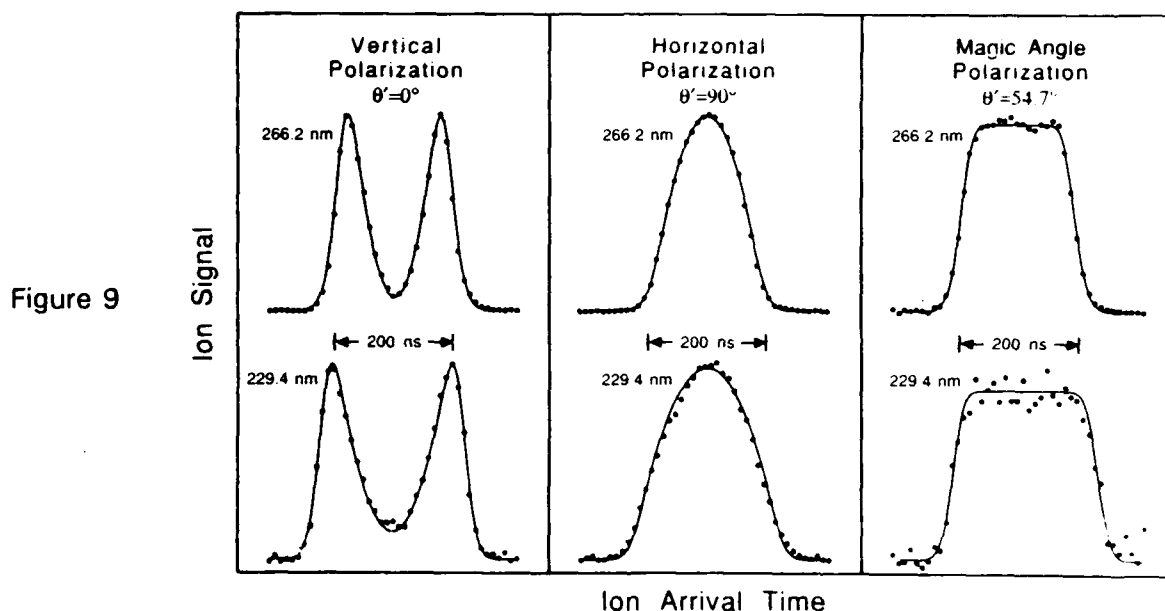


Figure 8

comparison, show that these two pathways are important in the decomposition of nitroethane, and we are currently collecting and analyzing more data at a number of wavelengths. The photodissociation cross section of nitroethane at 280 nm is only $3 \times 10^{-20} \text{ cm}^2$, corresponding to an extinction coefficient of $\epsilon = 10 \text{ l mol}^{-1} \text{ cm}^{-1}$. We have obtained excellent signals by averaging a few thousand laser pulses for even smaller cross sections using less than a mJ of photolysis light. This excellent sensitivity, which arises from our collecting and mass analyzing all of the ions produced in the efficient, energy selective photoionization near the threshold energy, allows us to work with the relatively small pulse energies that we obtain from tunable ultraviolet sources and not be limited to powerful fixed frequency lasers.

Energy selective ionization combined with time-of-flight mass spectrometry provides information about the disposal of energy into relative translation. Fragments that recoil toward the detector arrive sooner than those with no component of momentum in that direction while those that recoil away arrive later. Although this time difference is a small fraction of the total flight time, we can easily detect it in the shapes of the mass peaks. Figure 9 shows arrival time distributions of the iodine ions from electron impact ionization of



the iodine atoms formed in the photolysis of CH_3I at 266 nm (upper panel) and 230 nm (lower panel).¹⁰ Each panel shows the distribution for the photolysis laser being polarized parallel (vertical) or at a right angle (horizontal) or at the "magic angle" relative to the axis of the flight tube in the mass spectrometer. (These electron impact ionization data also illustrate the remarkable improvement of vuv photoionization over electron impact ionization. The data in the figure come from averaging 10,000 laser pulses, but we now obtain superior data with only about 500 laser pulses, and the CH_3I photolysis is now so easy to study that we use it

for calibration.) The shapes of the features are exactly analogous to those obtained in Doppler scanning of transitions.²⁸ Our technique and analysis approach is quite similar, except for minor technical details about mass spectrometer operation, to one developed contemporaneously by Houston and coworkers²⁹ using resonant multiphoton ionization of the fragments. The effect of kinetic energy release is most apparent for the laser polarized along the flight tube axis (left hand side of the figure). The separation of the two-maxima yields the kinetic energy release, which is the same at 266 nm as found in angularly resolved photofragmentation experiments³⁰ and is about 60% larger for 230-nm photolysis. The shape of the features also carries information about the anisotropy of the recoil distribution, and our measurement of $\beta = 1.6$ at 230 nm is the first determination at that wavelength.

We are using this ability to identify the masses, determine translational energies, and measure recoil anisotropies to unravel many details of the decomposition of nitromethane,¹² nitroethane,¹³ and nitrobenzene.¹⁴ For example, we are able to observe a relatively minor channel that produces CH_3NO in the photolysis of CH_3NO_2 , and we find little kinetic energy release or anisotropy. Our very new data on nitrobenzene show the utility of combining all of the features of this approach. We observe channels producing NO and NO_2 along with their corresponding fragments. These channels show very different amounts of kinetic energy release, and, by exploiting the "momentum matching" of the fragments, in which fragment pairs having the same momentum distribution have the same arrival time distribution, we can uniquely assign the channels. The NO production apparently occurs through a nitrite intermediate, which has been postulated but not observed directly for solution phase decompositions,³¹ and which occurs in the infrared multiphoton decomposition of some nitroalkanes.³²

The crucial features of our approach are the detection sensitivity and combination of mass and energy selection in the product detection. Because we collect all of the ions, we are able to work at lower laser fluences than required in fully angularly resolved experiments, but this sensitivity comes at the price of a reduction in the resolution of the recoil energy distribution. The potential of this approach lies in its ability to identify primary photofragmentation products by universal detection and to provide an assessment of the kinetic energy release at many different photoysis wavelengths.

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