Technical Description of Project and Results Supported by ONR-N00014-87-K-0546

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I. Introduction and Brief Outline of Main Accomplishments

This final technical report summarizes the work supported by contract #N00014-87-K-0546, "Selective Dissociation Pathways Induced by Local Electronic Excitation of Molecules ...". The cumulative support for a three year period beginning June 1, 1987 was $210,000. With permission of the project director, we obtained joint support from other sources, primarily the National Science Foundation, to enable us to achieve some of the results described herein.

Our scientific goal for the contract focused on investigating how local electronic excitation of a polyatomic molecule can result in selective decomposition channels over other energetically allowed ones. The possibility of inducing bond-selective chemistry following local electronic excitation has, for the most part, eluded study in the past because of the difficulty of detecting reactive primary products. The measurement of product velocity and angular distributions in our newly constructed crossed laser-molecular beam apparatus via a photofragment time-of-flight technique overcame this obstacle and incorporated specific capabilities crucial to elucidating the nonadiabatic transitions which result in particular dissociation pathways. Of central importance in our work described below is our success in understanding and generalizing methods for inducing bond selective chemistry via laser excitation. While Lee and coworkers previously showed that direct laser excitation to an excited potential energy surface repulsive in a specific bond could induce fission of that bond, this technique for inducing bond selective chemistry has not been widely utilized for two reasons. First, although selective C-Br fission resulted from excitation of the n(Br) -> σ^*(C-Br) transition in CH_2BrI photodissociation at 210 nm, the same excitation in C_2F_4BrI did not result in selective fission of the C-Br bond. Also, because repulsive electronic states are, for most bonds, inaccessible in the near UV, the technique was not suitable for the control of fragmentation pathways in many systems. Thus our work under this contract focused on developing new methods for controlling chemical fragmentation as well as elucidating the underlying mechanisms for inducing and for inhibiting bond-selective chemistry via electronic excitation.

Section II details the work supported by and results obtained under this contract. Section II.A. describes the capabilities of the state-of-the-art molecular beam apparatus constructed for these studies. Our work described in section II.B. demonstrates a new excitation mechanism for controlling chemical fragmentation, that of using electronic excitation localized on a particular functional group to favor the fission of a bond alpha to that group. In Sections II.C thru E, we describe three experiments which elucidate some of the intramolecular forces and couplings responsible for selective branching between energetically available dissociation pathways; we have found that intramolecular electronic energy transfer plays a central a role in all these systems. Of particular immediate interest to the ONR are the studies in Section II.E which show that the photodissociation of energetic materials, in this case nitromethane, produces exclusively highly electronically excited NO_2 products; a result with direct bearing on the explosive nature of many nitro compounds. These studies on influencing the selectivity of chemical reactions are fundamental to understanding and controlling reactions of polyatomic molecules both in the gas phase and in condensed media.

II. Detail of Work Completed During the Grant Period

A. Construction of a Crossed Laser-Molecular Beam Apparatus for Photofragment Velocity and Angular Distribution Analysis

A major effort in our laboratory in the last three years has been to design and construct a crossed laser molecular beam apparatus for the measurement of branching ratios between energetically allowed dissociation channels following selective electronic excitation. Originally funded entirely by the Office of Naval Research, this project has received supplementary support from our NSF grants in the last year and a half. Our apparatus, an improved version of one recently constructed in Yuan Lee's laboratory, is designed to allow us to address fundamental questions centering on how an initial electronic excitation may result in specific dissociation channels among many energetically allowed ones. The apparatus allows us to measure the branching between all energetically allowed photodissociation channels under collisionless conditions, not just those channels which produce fragments amenable to laser induced fluorescence or resonant multiphoton ionization detection. Thus we were able to pursue several studies which could not have been carried out with these other techniques which also detect nascent photofragments. In addition, the measurement of product velocity and angular distributions via the photofragment time-of-flight technique provides key information which allows us to assess the nature of the intramolecular forces, symmetry of initial transition, as well as timescale of the dissociation which resulted in the selective branching between energetically allowed fragmentation channels. Several key experiments completed in the grant period required the capabilities of this apparatus.

In the molecular beam experiments, we photodissociate the reagent molecules, cooled in a supersonic expansion, and measure the resulting photofragments' velocities and angular distributions. Neutral dissociation products scatter from the crossing point of the laser and the molecular beam with velocities determined by the vector sum of the molecular beam velocity and the recoil velocity imparted in the dissociation. Those scattered into the acceptance angle of the differentially pumped detector travel 44.1 cm to an electron bombardment ionizer and are ionized by 200 eV electrons. After mass selection with a quadrupole mass filter, the ions are counted with a Daly detector and multichannel scaler with respect to their time-of-flight (TOF) from the interaction region after the dissociating laser pulse.

The apparatus design incorporated several modifications to improve the resolution and background rejection for the experiments. As do all the apparati on which this design was based, the apparatus incorporates a triply differentially pumped detector, liquid nitrogen cooled ionization region insert with electron bombardment ionizer, a quadrupole mass filter, and Daly ion detector. The differential regions were modified to substantially reduce the background at 10 degrees from the molecular beam over that in the parent rotating source apparatus in Y.T. Lee's group. We also improved the design of the liquid nitrogen insert to allow us to use the full range of the hi-q head for each quadrupole range. As in the parent apparatus, the time-of-flight analysis of the molecular beam velocity may be done without venting the apparatus and the rotatable source is doubly differentially pumped and has mounted on it a liquid helium cooled slit to substantially reduce effusion from the differential regions into the detector. We modified the slit design to extend its usefulness to angles as close as 15 degrees between the detector and beam source; this was crucial in the experiments on selective S-H bond fission in methyl mercaptan described below, as the CH_3S^+ fragments do not recoil far from the molecular beam. The entire molecular beam line is bakeable and is fabricated of stainless steel to allow us to study the fragmentation channels of low vapor pressure condensables that are also moderately corrosive.

B. Inducing Selective Bond Fission via Excitation Localized at a Functional Group: C-Cl fission in Bromoacetylchloride at 248 nm

Upon completion of the molecular beam apparatus, we pursued a key experiment which demonstrated a new excitation mechanism for controlling chemical fragmentation, that of using electronic excitation localized on a particular functional group to favor dissociation at or near that group. Previous work by Butler, Lee and coworkers in 1986 showed that one can induce bond-selective chemistry by laser exciting a molecule to an electronic state that is directly repulsive in a specific bond in the molecule. In the new experiments, we excited the more commonly accessible transitions to bound electronic states localized at a particular functional group, with the goal of inducing selective fission of a bond at or near the functional group. We chose the bromacetylchloride system for study because local excitation at the carbonyl functional group promised the possibility of inducing fission of one of the bonds alpha to the carbonyl group; this would be a selective process in this system because simple thermal excitation would not result in fission of an alpha bond, it would give C-Br bond fission or a concerted elimination channel. We describe this system in more detail below.

The experiment uses our newly constructed crossed laser-molecular beam apparatus to study the competition between fragmentation pathways following excitation at the carbonyl functional group in bromoacetyl chloride. The experiment investigates whether selective fission of a bond next to the carbonyl group (an α bond) results from excitation of a bound to bound electronic transition localized at the carbonyl group. Textbooks of organic chemistry discuss the dominance of α-cleavage following this bound $n(O)\rightarrow\pi^*(C=0)$ excitation. Yet if this excitation is followed by internal conversion, the fission of the α bond over a weaker bond remote from the carbonyl group is contrary to the nearly universally successful unimolecular decay theories which calculate the branching between fragmentation pathways of vibrationally excited molecules assuming the energy is statistically distributed throughout the molecule. The study of the primary dissociation channel branching ratios, under collisionless conditions, of a molecule with a bond remote from the carbonyl group (in this system, the C-Br bond) which is weaker than the α-bond is key to resolving this apparent fundamental contradiction. The experiment was designed to determine whether α-bond cleavage results from bound $n(O)\rightarrow\pi^*(C=0)$ excitation, as suggested by textbooks of organic chemistry, or whether the energy is redistributed throughout the molecule and results in the fission of C-Br bond remote from the carbonyl group which is weaker than the α-bond. We measured both photofragment velocity distributions and angular distributions to assess the origin of the selectivity we observed.

The experimental results (see Figure 1), presently being prepared for publication, are as follows. Excitation at 248 nm in a region of the spectrum that excites overlapping $n(O) \rightarrow \pi^*(C=0)$ and $n(Br) \rightarrow \sigma^*(C\text{-}Br)$ transitions resulted in a competition between fission of the C-Cl bond next to the carbonyl functional group and weak C-Br bond fission, with a ration of C-Br fission : C-Cl fission of 1.1 to 1. The statistical prediction for the branching ratio is 30:1, so the excitation resulted in highly preferential fission of the

C-Cl alpha bond. We neither observed fission of the other alpha bond and nor any concerted elimination channels. The observed C-Cl bond fission would not have occurred with thermal excitation since the C-Br bond is weaker, so the data shows that excitation at the carbonyl functional group has resulted in the preferential fission of the C-Cl bond which is alpha to that group. The distribution of energies released to product translation (see Figure 1) in the C-Cl bond fission channel suggest that this selective dissociation pathway results from electronic coupling to the alpha bond and not from internal conversion. Some of the product signal observed which corresponds to C-Br bond fission with a large release to relative kinetic energy of the fragments surely results from the overlapping n(Br) → σ^*(C-Br) excitation, but the velocity of the Br atoms also shows a slow component that we ascribe to an indirect mechanism for fission of the weak C-Br that originates in the n(O) → π^*(C=0) transition. The anisotropy of the scattered products was measured to further elucidate the mechanism of the selectivity; we found the Cl atoms from C-Cl bond fission to have an anisotropy parameter of β=-1.0, exactly what would have been predicted if the molecule absorbed via the n(O) → π^*(C=0) transition and dissociated on a time scale short with respect to rotation of the molecular frame. The distribution of Br atoms from C-Br fission was also very anisotropic, suggesting that the selectivity is a result of dynamics on the singlet excited electronic potential surfaces rather from dynamics following internal conversion or intersystem crossing. Consideration of the probable relative height of the excited state barriers to C-Br fission and to C-Cl fission suggests that the dissociation on the excited singlet surfaces does not occur adiabatically, and that the origin of the selectivity is the stronger potential coupling between the diabatic n(O) → π^*(C=O) electronic state and the diabatic repulsive n(Cl) → σ^*(C-Cl) electronic state than between the n(O) → π^*(C=O) electronic state and the diabatic repulsive n(Br) → σ^*(C-Br) electronic state. Thus, we have found that the coupling between electronic states is central to determining the bond selectivity of a dissociation process, with intramolecular electronic energy transfer playing as pervasive a role in photodissociation as has been formerly elucidated for intramolecular vibrational energy redistribution. This experiment is most exciting as it shows that through local excitation at a functional group one can induce preferential fission of the α-bond, opening up an important way to control chemical reaction pathways.

To follow up on this system, we plan to investigate the branching between C-Cl fission and C-Br fission in CH_2BrCH_2COCl. We hope that by further removing the C-Br chromophore from the carbonyl group that we can completely supress the C-Br fission resulting from n(O) → π*(C=O) excitation. We are also investigating the competition between dissociation channels at 193 nm in the n(Br) → σ*(C-Br) absorption band in order to assess the contribution from that band in the 248 nm measurements. Finally, we have completed a study of the photodissociation of acetyl chloride; it dissociates by only C-Cl bond fission with an anisotropy of β=-1.0, in firm agreement with the model we have used to describe alpha bond fission in the bromo substituted compound.

C. Mechanism for the Dominant S-H Bond Fission in Methyl Mercaptan Photodissociated at 248 and 193 nm

A second system investigated under this contract showed selective fission of a stronger bond over a weaker bond, that of methyl mercaptan excited at 248 an 193 nm. At both wavelengths, the dominant fragmentation mechanism was S-H bond fission, requiring 80 kcal/mole, rather than C-S bond fission, requiring under 70 kcal/mole. Figure 2 shows the data obtained at 248 nm, where no significant branching to C-S bond fission was observed, and Figure 3 shows the data obtained at 193 nm, where a minor channel resulting in SH + CH_3 was observed. The anisotropy parameters measured at both wavelengths were near β=-.85±.1 for both channels, consistent with rapid dissociation following excitation from the A' symmetry ground state to the $1^1A''$ and $2^1A''$ states respectively at 248 and 193 nm. Again, the selectivity results from a nonadiabatic mechanism; the $2^1A''$ surface excited to at 193 nm is bound in the S-H stretch, yet the dominant dissociation pathway is fission of the S-H bond. The fast recoil velocities of the CH_3S fragment at 193 nm indicates the dissociation proceeds via coupling to the repulsive n(S)→σ*(S-H) diabat. We are preparing a short communication for publication on the results at 193 nm and are pursuing *ab initio* calculations of the first excited $^1A''$ state to better assess the mechanism for the selectivity at 248 nm.

D. The Influence of Parent Bending Motion on Branching at a Conical Intersection in the Photodissociation of CX_3I (X=H,D,F)

In 1990, we published our first experiment using our new crossed laser-molecular beam apparatus (we attach the reprint of this work which appeared in J. Chem. Phys.). The experiment was designed to probe the multidimensional nature of the coupling between Born-Oppenheimer potential energy surfaces; such coupling is pervasive in the dissociation of polyatomic molecules from excited electronic states and can result in branching between energetically allowed fragmentation pathways. The experiment measures the branching ratio between the two dissociation pathways as a function of the initial parent molecules' vibrational excitation. Excitation of parent vibrations prepares a molecule in the ground electronic state with different Franck-Condon overlap with the excited state potential energy surface; the resulting dissociative wavefunction can thus sample a different region of the coupled excited electronic surfaces. In the case we studied, that of the iodo- and trifluoroiodo- methanes, the radial derivative coupling between the two relevant dissociative excited electronic states is only non-zero at non-C_{3v} nuclear geometries on the excited state surfaces. By exciting molecules with nonzero quanta in e-symmetry bending vibration to the repulsive surfaces, we prepared a dissociative wavefunction with increased probability amplitude away from C_{3v} geometries. The experiment tested if this results in the dissociating molecules sampling regions of the conical intersection where the coupling is greater and brings about a change in the branching ratio between the two energetically allowed product channels.

We chose the model system of CF_3I for these studies based on a careful reexamination of the nature of the coupling between the $n \rightarrow \sigma^*$ dissociative electronic states in CX_3I (X=H,D,F) and the thermal accessibility of the bending modes in CF_3I. The manuscript attached first describes the failure of simple one-dimensional Landau-Zener models of the iodoalkane curve crossing in accounting for the observed iodine spin-orbit branching ratios in CD_3I versus CH_3I at 248 nm. Then, after reviewing calculations of the adiabatic potential energy surfaces in C_{3v} and in C_s geometry, it proposes a model which can explain the decrease in branching to the $I(^2P_{3/2})$ channel for CD_3I based on its smaller zero point bending motion. This model provided the basis for the experiment performed on CF_3I, which tests whether inducing bending in the parent by exciting it thermally results in an increase in the branching to the $I(^2P_{3/2})$ channel at the conical intersection. The experimental result showed that by vibrationally exciting the CF_3I prior to photodissociation we enhanced the branching to $CH_3 + I(^2P_{3/2})$ by a nearly a third (from an 0.13 quantum yield for that channel to an 0.17 quantum yield). Angular distribution measurements showed that the increase was indeed due to a change in the branching a the conical intersection and not simply enhanced absorption to the second electronic state. The success of this experiment opens up a world of exciting possibilities for utilizing vibrational excitation of the parent molecule prior to electronic excitation to allow control of the fragmentation pathways on coupled electronic states (not just changing the Franck-Condon overlap to access different regions of a single dissociative state).

E. Emission Spectroscopy of Photodissociating Nitromethane at 200 and 210 nm: The Exclusive Formation of Electronically Excited NO_2

The previous successful experiment in inducing bond-selective chemistry in my work with Yuan Lee utilized a system where one could laser excite the molecule to an electronic state that was directly repulsive in a specific bond in the molecule. In working toward extending this work to systems where one excites the more commonly accessible transitions to bound electronic states localized at a particular functional group, with the goal of inducing selective fission of a bond at or near the functional group, we investigated the photofragmentation pathways of nitromethane excited via a π to π^* excitation localized on the NO_2 functional group.[1] The experiment detected the emission from the dissociating molecule to probe the molecule during the bond fission dynamics. The C-N bond breaks via two distinct mechanisms, one of which could not be conclusively assigned in earlier molecular beam experiments. We were able to show that the slow methyl products from this second channel result from a direct dissociation pathway to $CH_3 + NO_2(2^2B_2)$, where the 2^2B_2 state has nearly 90 kcal/mole of electronic energy. Thus we have identified that both sets of photodissociation products of this energetic material results in the formation of NO_2 in excited electronic states; no NO_2 is formed in the ground state. The highly unusual exclusive production of electronically excited products likely lies at the root of the effectiveness of this energetic material as an explosive since electronic energy transfer is highly effective for transferring large amounts of energy upon a single collision. See the attached publication preprint for the full details of this work.

The experiment on nitromethane opened up the possibility of using the π to π^* excitation localized on the NO_2 functional group to induce bond selective chemistry in energetic materials containing nitro groups. We are presently continuing this effort by investigating the photodissociation pathways of nitrobenzene, as a prelude to attempting to induce bond selective C-N cleavage in nitro-iodobenzene (the C-N bond is several kcal/mole stronger than the C-I bond). Although the 248 nm dissociation of nitrobenzene evidences competing reaction channels that would occur thermally, such as the concerted elimination of HONO, the photodissociation of nitrobenzene in the 193 nm band should proceed by the strong predissociation of the$^1B_2(\pi\pi^*)$ electronic state by the the $^1B_2(n\sigma^*)$ state, as we observed in nitromethane at 193 nm, and yield the selective fission of the C-N bond. We have taken preliminary TOF spectra on this system and ave observed C-N bond fission. In in nitro-iodobenzene, we should be able in this way to induce fission of the C-N bond over the weaker C-I bond.

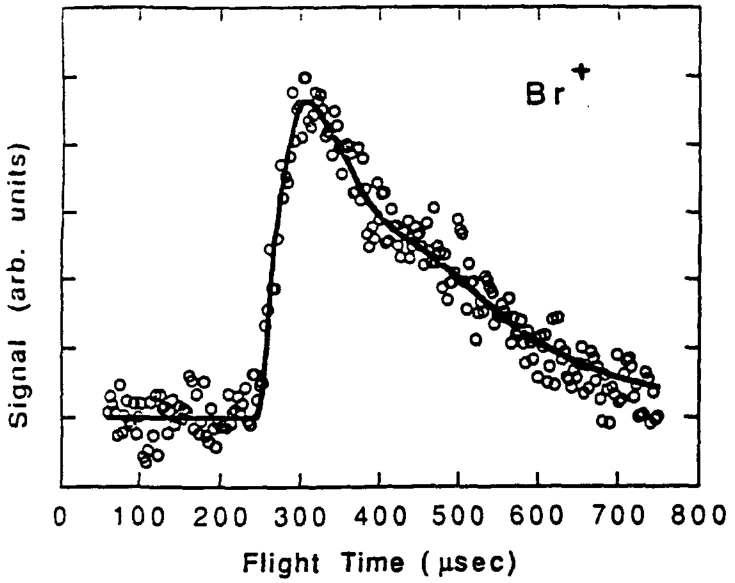
III. List of Publications Supported by the ONR

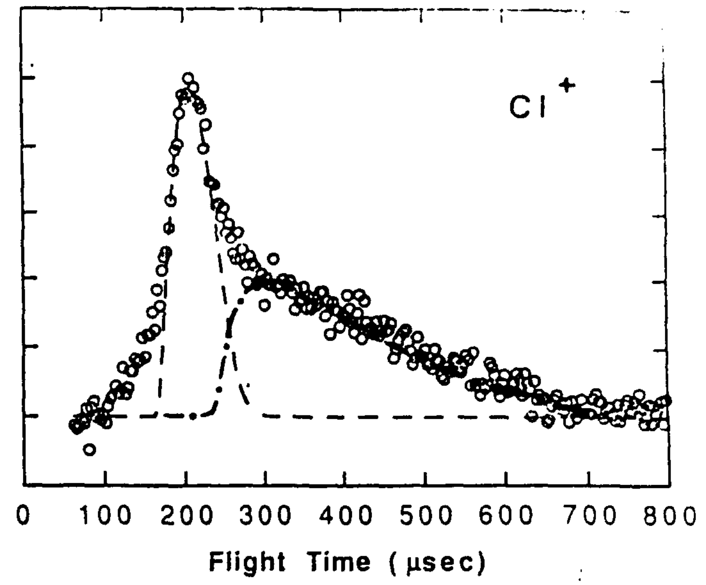
1. Polarized Emission Spectroscopy of Photodissociating Nitromethane at 200 and 218 nm, K.Q. Lao, E. Jensen, P.W. Kash, and L.J. Butler, J. Chem. Phys. 93, 3958 (1990).

2. The Influence of Parent Bending Motion on Branching at a Conical Intersection in the Photodissociation of CX_3I (X=H,D,F), M.D. Person, P.W. Kash, and L.J. Butler, J. Chem. Phys. 94, 2557 (1991).

3. The Nonadiabatic Competition Between S-H and S-C Bond Fission in the Photodissociation of Methyl Mercaptan at 248 and 193 nm, J.S. Keller, P.W. Kash, E. Jensen, and L.J. Butler, in preparation.

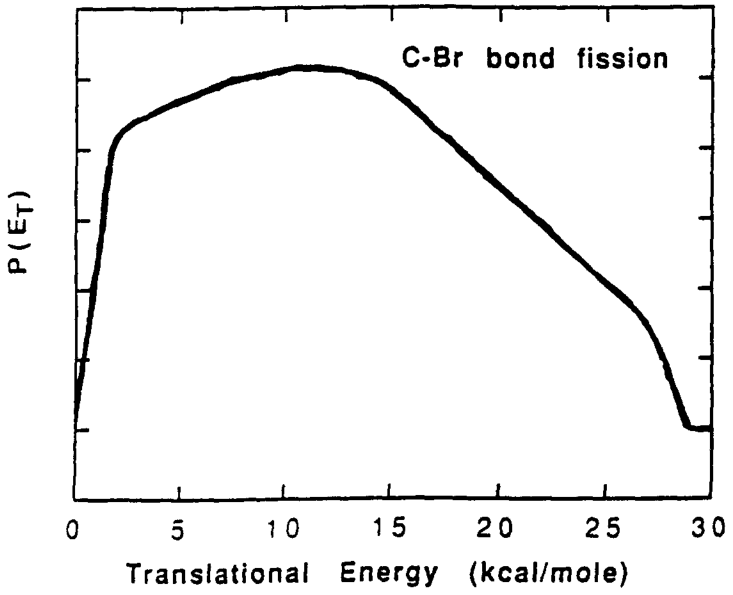
4. Selective α-Bond Fission in Bromoacetylchloride upon Local Excitation at the Carbonyl Functional Group via the $\pi^*(C{=}O) \leftarrow n(O)$ Electronic Transition, M.D. Person, P.W. Kash, S. Schofield, and L.J. Butler, in preparation.





Time-of-arrival of photofragments taken at m/e = 79. All the signal is assigned to Br atoms from C-Br fission. The P(E_T) for C-Br fission shown below was obtained by forward convolution fitting of the TOF spectrum. The Br photofragment anisotropy was measured to be approximately β = 0.75. The momentum matched fragments to the Br atoms appears at the Cl+ daughter ion in the spectrum shown to the right.

The signal at m/e = 35 arises from three sources. The time-of-arrival of the momentum matched CH_2COCl fragment from C-Br fission is obtained from the P(E_T) derived from the m/e = 79 data and is shown by the _ . _ fit. The fast shoulder at 150 μsec has a nonlinear power dependence so arises from secondary photodissociation. The remaining signal near 200 μsec arises from Cl atoms from C-Cl bond fission. The P(E_T) derived from fitting this Cl atom signal is shown below. The measured anisotropy for the Cl atoms is β = 1.0.



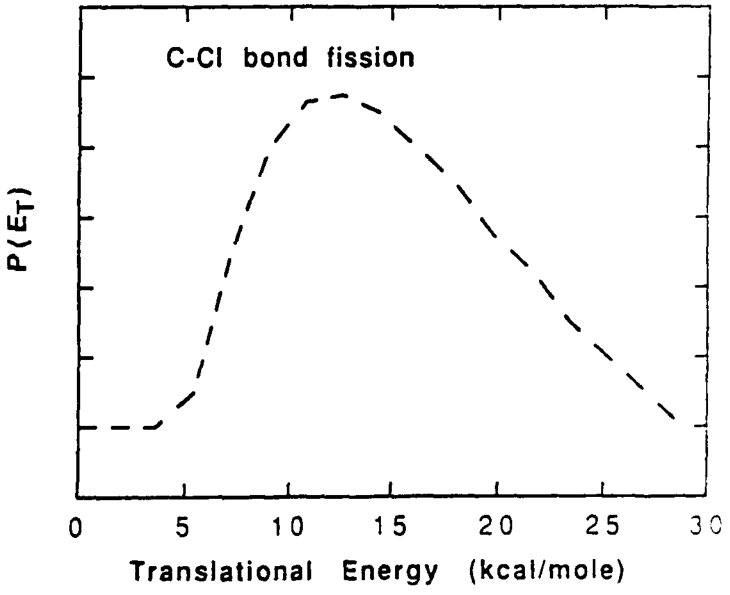
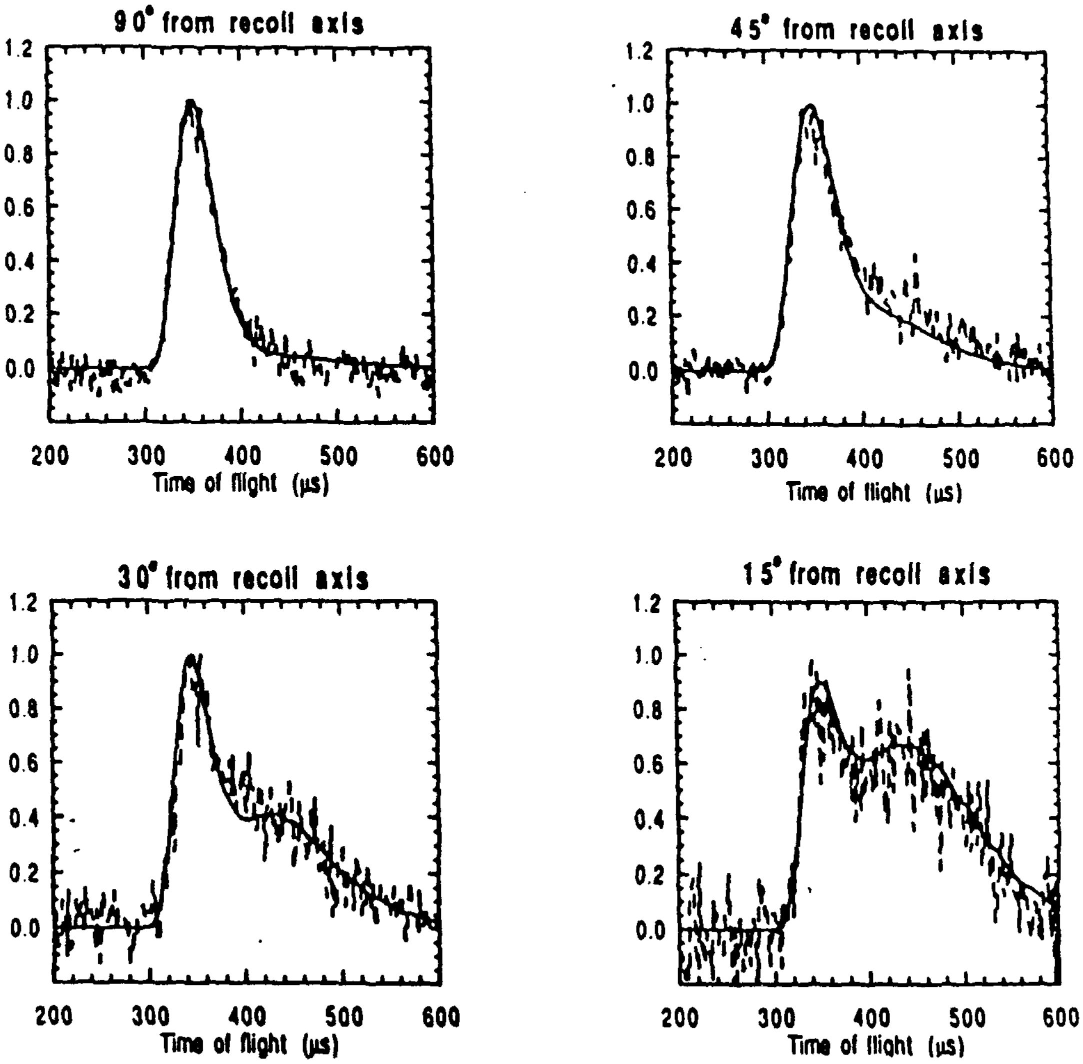


Figure 1

248 nm PHOTOLYSIS OF CH_3SH
TIME-OF-FLIGHT PHOTOFRAGMENT DISTRIBUTIONS
FOR m/e$^+$ = 47 (CH_3S^+)



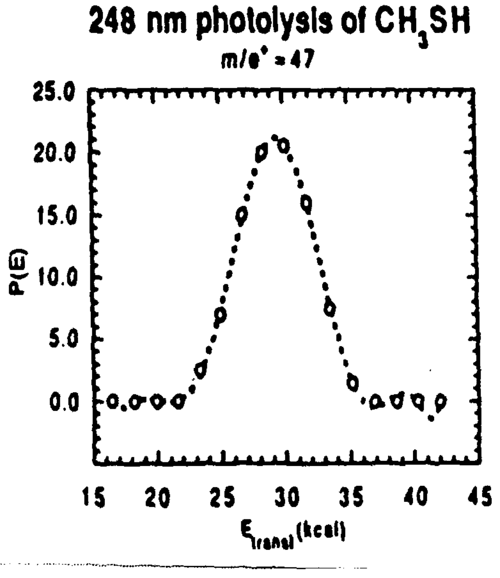
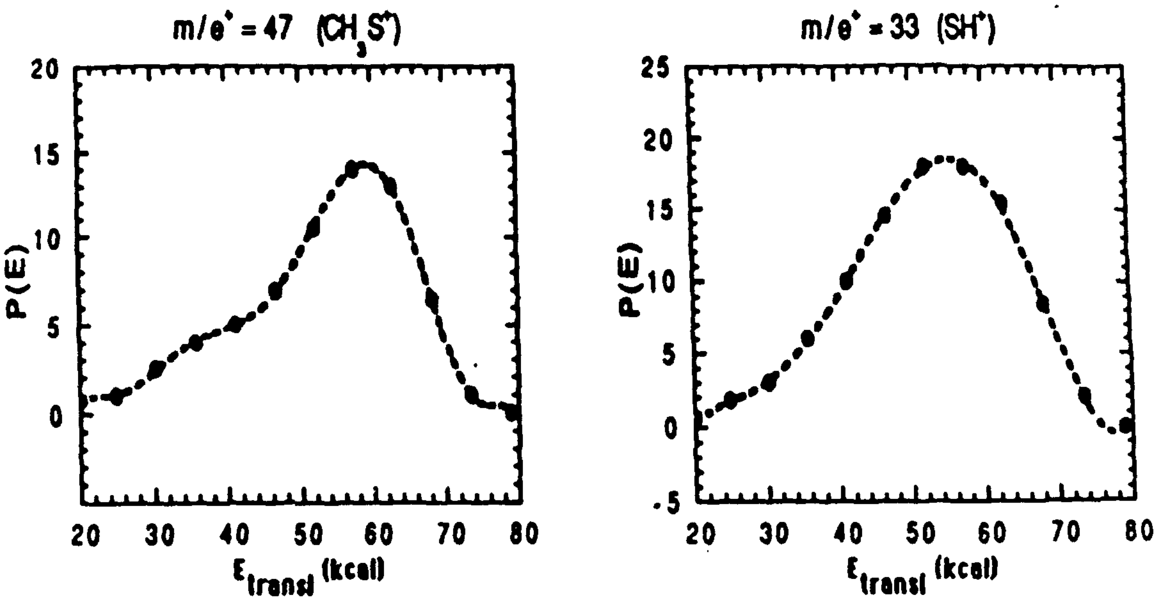


Figure 2

193 nm PHOTOLYSIS OF CH_3SH
TRANSLATIONAL ENERGY DISTRIBUTIONS



POLARIZED LASER PHOTOLYSIS YIELDS ANGULAR DISTRIBUTIONS OF PHOTOFRAGMENT

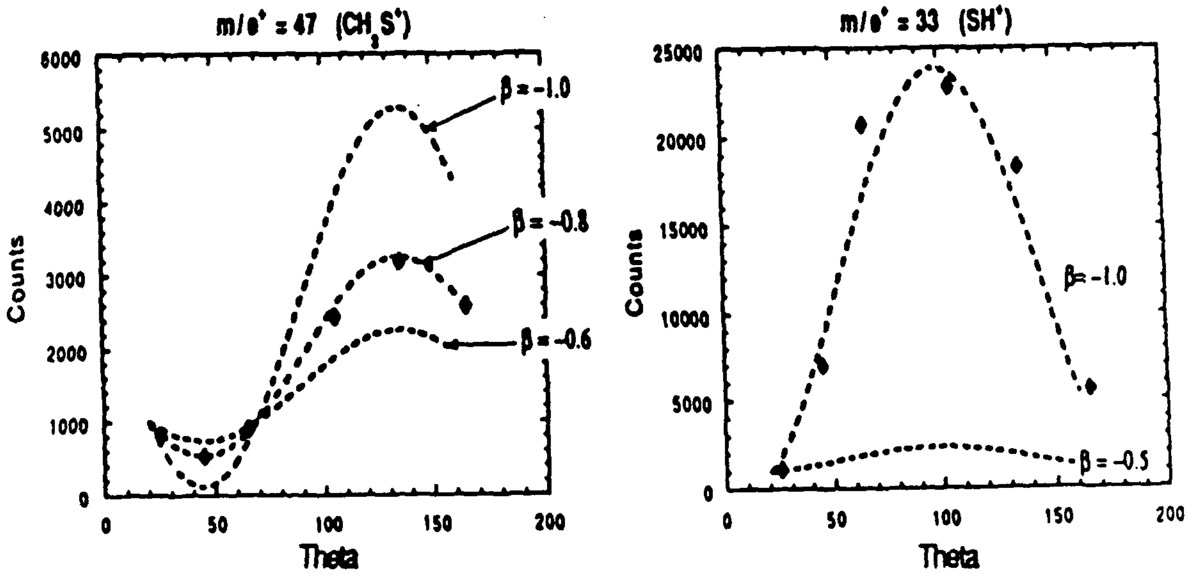


Figure 3