MOLECULAR BEAM STUDIES OF UNIMOLECULAR REACTIONS: Cl, F + C2H3Br

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MOLECULAR BEAM STUDIES OF UNIMOLECULAR REACTIONS:

Cl, F + C₂H₃Br

Richard J. Buss, Michael J. Coggiola, and Yuan T. Lee

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ABSTRACT

Several methods currently used to study unimolecular decomposition in molecular beams are discussed. We present experimental product angular and velocity distributions obtained for the reaction of F, Cl with C₂H₃Br. The mechanism by which conservation of angular momentum can cause coupling of the product angular and velocity distributions in dissociation of long-lived complexes is introduced.
Slightly over a decade ago, evidence for the existence of long-lived intermediates from reactive encounters of molecules in beams was presented at a Faraday Discussion meeting. This suggested the attractive possibility of studying the dynamics of unimolecular decomposition by the measurement of angular and velocity distributions of products in a collision free environment after preparing long-lived complexes by chemical activation. In the years since, a great number of reactions which appear to proceed via persistent complex have been studied in molecular beams. Although the early experiments frequently employed thermal beams and, hence, provided poor characterization of the collision energy, later refinement in beam techniques, especially the use of supersonic nozzle sources, has greatly increased the effectiveness of the method in providing insight into reaction dynamics.

More recently, a new technique, infrared multiphoton excitation in beams, in which molecules are excited under collision free conditions by absorbing tens of photons during an intense single laser pulse, has proven to be an excellent way to prepare excited molecules and to gain dynamical information about unimolecular decomposition. The study of some forty reactions ranging from simple bond rupture to three and four center eliminations has revealed trends which can likely be generalized to large classes of unimolecular decay.
These two methods, chemical activation and multiphoton excitation, differ substantially in several important respects. As a consequence the information obtained is complementary rather than overlapping.

The nature of the excitation process places limitations on the certainty with which we know the total energy of the dissociating molecules. With chemical activation in crossed beams, the total energy is simply the sum of internal energy of the reactants, energy released in formation of the new chemical bond, and the collision energy. The principal uncertainty, arising from the spread in collision energies, can be reduced to a small fraction of the total energy. With the use of two supersonic nozzle beams, the collision energy may typically be defined to FWHM = 5-10 kJ mol⁻¹ which is often only 2-3% of the total excitation energy of the complex. This excellent energy characterization, combined with the variability of collision energy obtainable by seeding of the reactants with rare gases, make this technique a sensitive probe to the dynamics of unimolecular decomposition.

In sharp contrast, infrared multiphoton absorption produces excited molecules with a spread in excitation energies which can be an exceedingly large fraction of the average total energy. This problem is fundamental to the process, being governed by the mechanism of absorption of many photons. In the sequential absorption of
photons, after an initial excitation through a region of discrete transitions, the molecule is excited to a region referred to as the quasi-continuum. The density of states, here, is sufficiently high that all transitions are near-resonant, essentially independent of laser frequency. A fairly adequate description of the population distribution of each level is given by a set of rate equations with transition rates depending on laser intensity, energy level dependent infrared absorption cross sections and density of states. The result is somewhat similar to thermal excitation with a simple dependence of average excitation level on the energy fluence of the laser pulse. When the laser fluence is sufficient to drive the molecules above the dissociation threshold, an extra term must be added to the rate equations, to account for depletion by dissociative processes. At some high excitation level, the dissociation rate becomes much faster than the rate of excitation and population of higher states will not be significant. For a large molecule with high density of states around the dissociation levels, the unimolecular rate constant will increase gradually with excitation. Substantial dissociation will occur over a large range of levels. SF$_6$, for example, is calculated to undergo detectable multiphoton dissociation (MPD) at levels from 4 to 13 photons above threshold, the total energy in the system then being defined to FWHM = 60 kJ mol$^{-1}$ or about 15%. For smaller molecules, in which the rate constant increases more rapidly with excitation energy, the uncertainty in energy of the
reacting molecules will be much narrower since most of the molecules dissociate from a level only a few photons above threshold.

The degree to which angular momentum affects the outcome of the unimolecular decay is also considerably different for the two processes. In both cases, cooling of the rotational degrees of freedom during supersonic expansion of the beams results in a low and relatively well-defined rotational temperature. In the bimolecular collision which produces the chemically activated species, orbital angular momentum can be very large, even at thermal energies, and sometimes dominating in its effects on the product translational energy distribution. Although the theoretical treatment of the effect of angular momentum on product energy distributions is fairly well developed, it remains a fundamental limitation in the analysis of this type of experiment that the probability of formation of the complex as a function of impact parameter which governs the distributions of angular momentum of the complexes is indeterminant. In consequence, it is incumbent on the theory to account correctly for angular momentum conservation, though this may require knowledge of dynamical features of the reaction, such as preferred orientation of reactants.

In MPD, angular momentum is found to play a much less significant role in the unimolecular decay. The depletion of low translational energy product expected for reaction with an exit channel centrifugal barrier associated with rotational motion is not observed in halogen atom detachment reactions using this technique. This indicates that the absorption of some forty photons does not appreciably increase
the originally low average rotational energy. This greatly facilitates
the comparison of product translational energy with statistical
calculations.

The two methods lend themselves, most conveniently, to the study
of different chemical systems. MPD in beams has been used extensively
to study unimolecular decay of closed-shell molecules. In particular,
molecules with huge barriers to dissociation, for example, the three-
center elimination of HCl from CHF₂Cl with approximately 225 kJ mol⁻¹
barrier, are accessible with the energy fluence attainable in a high
power CO₂ laser pulse. Indeed, MPD has been applied to systems ranging
from such highly endoergic reactions to the nearly thermoneutral
dissociation of ammonia dimers.

Chemical activation has been applied principally to the investi-
gation of open-shell systems. The addition of a radical species, eg.
halogen atom, oxygen atom or methyl radical, to an unsaturated hydro-
carbon to produce an excited radical intermediate constitutes the
majority of long-lived complex reactions studied in crossed beams.
The study of closed-shell systems by radical-radical combination
collisions should become more frequent as these beam sources are
developed.

A final aspect which distinguishes MPD from chemical activation
is the time domain of the reactions. The multiphoton excitation
always raises the molecules to a level at which the dissociation
rate approximately equals the up-pumping rate. For the typical
energy fluences attainable in a 50 nsec CO₂ laser, this fixes the
upper limit of the average lifetime of the system at close to a nano-
second, fairly independent of the chemical nature of the molecule or
type of dissociation process occurring. Using chemical activation,
with its rapid deposition of bond-formation energy into the molecule,
systems with average lifetimes shorter than a picosecond can be
studied using the rotational period of the complex as an indicator.
The method offers the possibility of finding a range of applicability
of the statistical model for unimolecular decay. By studying reactions
with a wide range of lifetimes, one can hope to place a bound on the
time necessary for memory of the excitation event to be lost, though
this time would undoubtedly be dependent on the exothermicity of the
reaction, the stability and complexity of the intermediate.

The MPD of a large number of systems in which a single halogen
atom is detached from a halocarbon has convincingly demonstrated the
statistical nature of the process. The primary pathway for decom-
position is always found to be the statistically most favorable. The
product translational energy distribution peaks at zero energy and
has the correct statistical fall-off. Because the molecules under-
going dissociation have an average lifetime around one nanosecond
after absorbing the final photon, we can conclude that the time for
energy to be effectively randomized over all internal degrees of
freedom should be much less than one nanosecond. Unfortunately, due
to the limitation in the multiphoton excitation, it is not likely
that these experiments will reveal exactly how fast the energy
randomizes in the highly excited molecules.
In order to investigate the extent of intramolecular relaxation before chemical decomposition in a shorter time span than that of multiphoton decomposition, reactions of Cl and F with \( \text{C}_2\text{H}_3\text{Br} \) have been carried out in molecular beam experiments. In these chemical activation studies, as mentioned before, the product translational energy distributions, henceforth denoted \( P(E') \), may be strongly influenced by angular momentum conservation, as well as by any potential barrier in the exit channel. The substitution reactions of fluorine and chlorine atoms with vinyl bromide are known to proceed with negligible potential barrier to bromine elimination. Angular momentum effects are large, though, and careful consideration of this is necessary in order to draw conclusions concerning the statistical nature of the process. Some important consequences of angular momentum, especially the coupling of angular and energy distributions of products will be discussed below.

EXPERIMENT

The crossed beam scattering apparatus and data acquisition methods used for these experiments has been described in detail.\(^5\) The supersonic fluorine beam was produced by thermal dissociation of a 1% \( \text{F}_2 \) in argon mixture in a resistively heated nickle oven at about 1080°K. The chlorine source was similar, except the oven was high density graphite, and the mixture, 10% \( \text{Cl}_2 \) in argon, was heated to 1400°K. Vinyl bromide, undiluted, at a pressure of 250 torr was expanded from a 0.2 mm glass nozzle at room temperature. Time of flight characterization of the beams gave the information listed in
The spread in collision energies is determined from these parameters to be FWHM = 7.1 kJ mol$^{-1}$ or 5.6% of the total energy for the chlorine reaction and FWHM = 4.2 kJ mol$^{-1}$ or 2.2% of the total energy for the fluorine reaction. The laboratory angular distributions of product, shown in Fig. 1, were obtained by repeated scans with 100 second counts at each angle. In the fluorine experiment, elastic scattering of impurity from the secondary beam contributed to the signal at angles greater than 30°. The intensities at these angles were corrected by subtracting from them, the signal measured with a pure hot argon beam replacing the F/Ar mixture. The product flux distributions shown in Fig. 2 and 3 were obtained by the cross correlation time of flight method. The best fit lines in Fig. 1, 2 and 3 were obtained using the ratio method iterative deconvolution procedure. The angular and velocity data have been combined to produce center of mass flux contour plots shown with the canonical Newton diagram in Fig. 4 and 5.

RESULTS AND DISCUSSION

The product angular distribution provides some information about the average lifetime of the reaction intermediate. The existence of symmetry of the product angular distribution about 90° in the center of mass reference frame, reflects a complex lifetime which is longer than the average rotational period of the molecule. An approximation to the mean rotational period is obtained by assuming a geometry for the complex to generate moments of inertia, and estimating the average
angular momentum of the complex. For the chlorine reaction, the mean rotational period is estimated to be 3 ps. The RRKM theory predicts a mean lifetime of 0.1 ps, though this number is rather sensitive to the frequencies used in the calculation. We would expect, then, that the reaction should not exhibit forward backward symmetry if its lifetime is entirely determined by a statistical distribution of internal energy. In the laboratory reference frame, for this reaction, the back-scattered product is de-emphasized in the center of mass to laboratory transformation, and most back-scattered product is also beyond the range of the detector. The single datum at 99° was compared with a detailed calculation in which the RRKM-AM P(E’) calculated for a range of collision energies and weighted by calculated total cross sections, with assumed forward backward symmetry, was transformed to the laboratory reference frame. The calculated intensity at 99° was a factor of 1.7 times the observed intensity, or six standard deviations away, thus strongly suggesting that the lifetime is indeed less than a rotational period. Were the product to exhibit a longer lifetime than statistical, one might conclude that there was decoupling of the reaction coordinate from the major excitation modes causing a bottleneck in the energy transfer or possibly a slow atomic migration limiting the rate of decomposition. The statistical calculations for the fluorine reaction also predict asymmetry in the angular distribution, but the impurity in the vinyl bromide beam prevented detection of any back-scattered vinyl fluoride product. Although use of the rotational period for measuring the lifetime
in these experiments provides only the crudest estimate of the statistical behavior of the system, the product translational energy distribution gives a far more sensitive test, if careful attention is paid to the treatment of angular momentum conservation.

One of the most interesting observations in the reaction of chlorine and vinyl bromide is the presence of coupling of the product angular and energy distributions. In Fig. 4 the dashed line through the peak in product flux at $0^\circ$ is contrasted with the dotted line through the observed peak at each center of mass angle as the average translational energy of the products becomes smaller at wide angle. Considerable attention has been paid to this type of coupling arising in direct reactions with a large impulsive force in the exit channel. The effect has been observed in a number of alkali atom reactions with halomethanes, but in the analysis of long lived complexes, it has always been assumed that the energy distribution is independent of scattering angle. In fact, angular momentum conservation is also expected to create such coupling in reactions proceeding through long-lived complexes. When the impact parameter is large, the orbital angular momentum will often dominate the molecular angular momentum in the reaction, the angular momentum of the activated complexes will be highly polarized, perpendicular to the relative velocity, and a large fraction of the initial relative kinetic energy will become rotational energy of the complex as a consequence of the conservation of angular momentum. If most of the angular momentum of the complex is carried away as orbital angular momentum of the products, the product
angular distribution will be strongly peaked in the forward and backward direction and most of the rotational energy of the complex will be converted to translational energy, such that the product energy distribution will be shifted to higher average energy than that released along the reaction coordinate from the sharing of excess vibrational energy. On the other hand, if the impact parameter is small, the orbital angular momentum will no longer dominate the molecular angular momentum. Consequently, the angular momentum of the complex will be distributed more isotropically due to random orientation of the molecular angular momentum of the reactants and the angular distribution of products will tend to be more isotropic. In addition, with a small impact parameter, most of the initial translational energy will become vibrational energy of the complex, the rotational to translational energy release in the formation of product molecules is less important and the energy distribution will be closer to what one would expect from simple statistical considerations with a translational energy distribution peaking closer to zero energy. This coupling of angular and energy distributions due to the constraint of the conservation of angular momentum should be observable in the experiment if the contribution from large impact parameter collisions does not overwhelm the small impact parameter collisions.

A simple calculation to demonstrate this effect is shown in Fig. 6. The contour map of product flux distributions compare a calculation of RRKM-AM product energy distribution decoupled from the angular distribution with one including coupling. The latter
calculation is the sum of fifty distributions in which \( P(E') \) and \( P(\theta) \) are varied together considering the magnitude and polarization of angular momentum, simulating the range of impact parameters expected in the chlorine reaction with vinyl bromide as shown in Fig. 7. Despite the lack of sophistication of the model, the major features of this coupling are evident. At 0° the flux peaks at higher velocities with coupling while the reverse is true at 90°. The effect would be less noticeable in reactions with larger cross sections in which large impact parameter collisions dominated. Of course, this demonstration of the existence of coupling in the angular and energy distribution of product molecules in the long-lived complex does not imply the existence of a long-lived complex between chlorine and vinyl bromide.

Comparison of the product energy distributions with RRKM-AM calculations for the two reactions is shown in Fig. 8. The experimental curve for the chlorine reaction is the average \( P(E') \) for the product scattered between 0 and 90 degrees in the center of mass frame. Parameters used in the calculations are shown in Table II. The vinyl chloride product from the chlorine reaction is seen to be in poor agreement with the statistical calculation, the product energy being substantially higher than calculated. Extensive testing with the model demonstrated that the failure is not the result of the chosen vibrational frequencies, the energetics, or the choice of maximum centrifugal barrier \( B_m' \) in the angular momentum treatment. The calculated \( P(E') \) is very insensitive to the first and second within reasonable range of the parameters. The dotted curve is produced with the para-
meter $B'_m$ having been set at an unreasonably high value, 60 kJ mol$^{-1}$, beyond which its effect is negligible.

There are two principle explanations for the discrepancy observed. The first is the much-discussed possible failure of the energy randomization hypothesis. The lifetime for this reaction is calculated by the statistical theory to be approximately 0.1 ps. It would not be improbable that this reaction is beyond the scope of a unimolecular decay theory since, if statistical theory is applicable here, intramolecular energy transfer must be faster than 0.1 psec. The second explanation is that the treatment of angular momentum is inadequate. The theory assumes a distribution of angular momentum which is linear in impact parameter with a cutoff determined by the long range forces. In practice, the relative cutoff for entrance and exit channel has been treated as a variable to obtain best fit. The linearity with impact parameter may be questioned. For this reaction, dynamical constraints may require that the atom attack at the double bond which is removed from the center of mass of the vinyl bromide. Approach at small impact parameter could be less favorable for reaction. A simple calculation based on this idea suggest that the angular momentum distribution might be more nearly quadratic in impact parameter. Assuming this distribution, the statistical calculation is found to fit the observed $P(E')$ quite well, though this is likely fortuitous. In the fluorine reaction, again, the agreement with theory is poor. While the experimental energy distribution below 5 kJ mol$^{-1}$ has large uncertainty resulting from the elastic impurity in the
C$_2$H$_3$Br beam, it is clear that the observed intensity of both low and high energy product is reduced. This is not easy to explain with a simple model and will probably require more information about dynamical effects of the potential energy surface for a thorough understanding, but it is quite clear for this system that the reaction lifetime is shorter than the intermolecular relaxation time.

SUMMARY AND CONCLUSION

McDonald and coworkers$^{10}$ have measured the infrared chemiluminescence from these reactions. They find that the product vibrational energy distribution is statistical for the fluorine reaction and non-statistical for the chlorine. While an earlier crossed beam study of the chlorine reaction using a beam of chlorine atoms with a thermal velocity distribution$^{11}$ seemed to indicate that product translation was statistical, our higher resolution results suggest that product translational is not statistical in either reaction. One explanation for the discrepancy for the fluorine reaction lies in the different energetics of the two systems. The greater exothermicity of the fluorine reaction leaves about 170 kJ mol$^{-1}$ in internal excitation of the product compared to about 60 kJ mol$^{-1}$ for the chlorine reaction. The chemiluminescence experiment measures the product emission milliseconds after reaction. If the vibrational energy is large enough that the molecule is above the ergodic limit, even if the initial distribution is not statistical, energy will be redistributed before the emission of the infrared photon is observed. Perhaps the higher internal excitation of the vinyl
fluoride product allows randomization before the emission is detected while the vinyl chloride product retains its non-statistical distribution. The lifetime of the activated complex in the fluorine with vinyl bromide reaction is only 0.05 psec, according to statistical theory. If such a treatment is applicable, as implied in the chemiluminescence experiment, the intramolecular energy transfer has to be faster than 0.05 psec which is highly unlikely.

The two techniques of MPD and chemical activation in beams are seen to produce complementary results. MPD has demonstrated that, without exception, energy appears to be randomized in the nanosecond time period of the reaction. Chemical activation in beams has revealed non-statistical effects appearing for reactions with sub-picosecond lifetimes. These observations are not in contradiction to the general conclusion obtained by Rabinovitch and coworkers\textsuperscript{12} that the intramolecular relaxation time of highly excited molecules is on the order of several picoseconds. The lifetime range available with chemical activation, together with its good energy specification should make it the method of choice for investigation of the efficiency of intramolecular energy transfer and detailed dynamics of unimolecular decay. Nevertheless, the MPD method should prove valuable for the study of exit channel dynamical effects in the highly endoergic three and four-center elimination reactions.
ACKNOWLEDGEMENT

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REFERENCES


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FIGURE CAPTIONS

Fig. 1. Laboratory angular distribution of vinyl fluoride product from the reaction $\text{F} + \text{C}_2\text{H}_3\text{Br} \rightarrow \text{Br} + \text{C}_2\text{H}_3\text{F}$, above, and vinyl chloride product from the reaction $\text{Cl} + \text{C}_2\text{H}_3\text{Br} \rightarrow \text{Br} + \text{C}_2\text{H}_3\text{Cl}$, below. The solid lines are best fits obtained by the ratio deconvolution method of Siska.

Fig. 2. The vinyl chloride product flux distribution measured at 15 laboratory angles. Solid lines are best fits obtained by the ratio deconvolution method. Dashed lines connect data points for clarity.

Fig. 3. The vinyl fluoride product flux distribution at 4 laboratory angles. Lines are best fit calculated curves.

Fig. 4. Center of mass $\text{C}_2\text{H}_3\text{Cl}$ product flux, deconvoluted for beam velocity spread, shown with the most probable Newton diagram. The dotted line is through the peak flux at each center of mass angle. The dashed line is at constant center of mass velocity $580 \text{ m s}^{-1}$ for comparison.

Fig. 5. Contour map of center of mass $\text{C}_2\text{H}_3\text{F}$ product flux, shown with the most probable Newton diagram.

Fig. 6. Model calculation of product flux distributions. Dashed curves are generated from a single RRKM-AM $\text{P}(E')$ with a single angular distribution. Solid curves are the sum of fifty $\text{P}(E')$ with coupled $\text{T}(\theta)$ distribution.

Fig. 7. $\text{P}(E')$ and $\text{T}(\theta)$ used to compare effect of angular momentum coupling. Shown are the RRKM-AM distributions for the uncoupled calculation. Also shown are three $\text{P}(E')$ and
T(θ) for orbital angular momentum $L = \ell \hbar$.

Fig. 8. Product translational energy distribution. Solid curves are experimental. Dashed curves are RRKM-AM with $B'_m$ determined by $C_6$ constants. Dotted curves show calculations with $B'_m$ increased to unphysically large values.
Fig. 1

LAB ANGLE, ° deg.
\[
\text{Cl} + \text{C}_2\text{H}_3\text{Br} \rightarrow \text{Br} + \text{C}_2\text{H}_3\text{Cl}
\]

\[E = 20.0 \text{ kJ mol}^{-1}\]

**Fig. 2**
\[ F + C_2H_3Br \rightarrow Br + C_2H_3F \]

\[ E = 11.5 \text{ kJ mol}^{-1} \]

\[ \Theta = 3.0 \]

\[ \Theta = 2.0 \]

\[ \Theta = 0 \]

\[ \Theta = 1.0 \]

LABORATORY VELOCITY / 100 m s\(^{-1}\)

FLUX / ARBITRARY UNITS

Figs. 3

YBL 7811-13381
Fig. 5
Fig. 7 XBL 7812-13224
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.