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Author
Sudbo, Aa.S.

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Aa. S. Sudbø, D. J. Krajnovich, P. A. Schulz,
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MOLECULAR BEAM STUDIES OF
LASER INDUCED MULTIPHOTON DISSOCIATION

Aa. S. Sudbo\textsuperscript{†}, D. J. Krajnovich\textsuperscript{*}, P. A. Schulz\textsuperscript{†},
Y. R. Shen\textsuperscript{†} and Y. T. Lee\textsuperscript{*}

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California, Berkeley, California 94720

\textsuperscript{*}Also associated with the Department of Chemistry, University of California, Berkeley.

\textsuperscript{†}Also associated with the Department of Physics, University of California, Berkeley.
A.1 INTRODUCTION

Laser-induced multiphoton dissociation (MPD) of molecules is a collisionless unimolecular process. In the early studies, the collisionless nature of the process was inferred by the observation of instantaneous luminescence from the dissociation products following laser excitation and by the observation of linear pressure dependence of the dissociation yield at sufficiently low gas pressures /A.1-4/. The experiments were done in gas cells in which excitation may be assumed collisionless if the laser pulse is much shorter than the mean free time between collisions of the molecules. Even so, after the laser pulse is over, molecular collisions in the gas cell are still unavoidable, leading to possible collisional dissociation of excited molecules and chemical reactions among dissociation products and excited parent molecules. Thus, it is generally recognized that the primary dissociation fragments cannot be unambiguously identified in the gas cell experiments.

The best way to study a collisionless process is of course in a collisionless experiment. A molecular beam method is therefore most appropriate for the study of MPD. Indeed, observation of infrared MPD in a molecular beam provides the most direct evidence that the process is collisionless /A.5/. The use of a mass spectrometer to detect the dissociation fragments from the beam allows us to identify the primary dissociation products in a straightforward way /A.5,6/. The latter information is in fact of great fundamental importance for the understanding of MPD, because it reveals whether there is
any correlation between the pattern of molecular dissociation and the vibrational mode through which the initial excitation is attained.

With a sophisticated molecular beam apparatus, which we shall describe later in the chapter, the angular and velocity distributions of the fragments can also be measured. From these measurements, much additional information about the dynamics of MPD can be deduced.

There are a number of important questions aside from major dissociation fragments and channels that need to be answered before a reasonable physical understanding of MPD can be achieved.

(1) What is the excitation mechanism? How does a molecule get excited through the discrete levels into the quasi-continuum states and then through the quasi-continuum into the dissociative continuum states? Does the excitation energy remain in the vibrational mode being excited or get quickly randomized into other modes as the level of excitation increases? How many photons does each molecule absorb before dissociation, or equivalently, what is the average excitation level from which a molecule will dissociate? What eventually limits the level of excitation?

(2) Through which channel (or channels) does the molecule dissociate and how does this depend on the laser excitation? Is the major dissociation channel in MPD different from that in thermal decomposition? What is the dissociation rate of a molecule and how does it depend on the level of excitation? Can competing dissociation channels exist with dissociation rates depending on laser excitation?
(3) What is the dynamics of dissociation? How does the energy available to the fragments distribute itself among the various degrees of freedom (translation, rotation, and vibration) of the fragments? Can the fragments absorb more laser energy and undergo a secondary MPD?

Most of these questions are usually difficult to answer from the analysis of final products in the gas cell experiments. However, as we shall see in this chapter, they can be and have been answered by measuring angular and velocity distributions of the fragments in the molecular beam experiment. In addition to the molecular beam experiments, the newly developed laser induced fluorescence technique for detecting a small number of molecules has been used to detect dissociation fragments from collisionless MPD in a low-pressure gas cell /A.7-12/. Because of the good spatial and temporal resolution of the probing pulse, this technique can also yield information on the dissociation dynamics of the fragments. In principle, this detection method sometimes is even superior to the usual mass spectrometric detection method used in most molecular beam experiments in the sense that it can also measure the rotational and vibrational energy distributions in the fragments. In practice, however, this technique is limited to some smaller fragments by the fact that the optical transitions of many larger dissociation fragments are either not known, too complicated, or cannot be reached by the available probe laser.

As has been stressed in other chapters, MPD is isotopically selective. It has also been proposed that MPD is mode-selective, that is, the excitation energy should remain to a large extent in the vibrational
mode being excited. If this were true, the dissociation products could be different from those expected in thermal decomposition, and application of MPD to chemical synthesis could lead to a revolutionary change in the field. So far, however, aside from some erroneous conclusions, no concrete evidence of mode-selective MPD has been reported.

The molecular beam experiments on many molecules described here have shown that in the infrared MPD process the rate of intramolecular energy transfer of dissociating molecules is faster than the rate of dissociation, such that the statistical theory of unimolecular decomposition (A.13) can be used to describe the dissociation of excited molecules satisfactorily. This is not really surprising, as will be discussed later, in view of the fact that the energy deposition rate as well as the rate of dissociation is rather slow compared with intramolecular energy transfer rates. Indeed, the statistical theory, used convincingly to explain our molecular beam experiments, is the key to answering most of the questions concerning the dynamics of MPD. It also allows us to establish a simple and reliable phenomenological model which enables us to understand and predict the MPD process more quantitatively.

In this chapter, our emphasis is on the study of MPD in a molecular beam with high-power infrared lasers. We shall first review the theory of unimolecular dissociation and the theory of multiphoton excitation of molecules. We shall then describe the experimental apparatus and the experimental results, followed by a thorough discussion on the results, the interpretation, the various aspects of the problem, and our present understanding of the MPD process.
A.2 THEORY

The infrared multiphoton dissociation of molecules can be considered as a multiphoton excitation process followed by a dissociation process. In the multiphoton excitation, the energy deposition in the molecule, after initial excitation over discrete energy levels, is mainly through stepwise incoherent one-photon transitions /A.14/. A simple phenomenological model using a set of rate equations can describe the time-dependent excitation of the molecules to and beyond the dissociation level. Prior to dissociation, the energy deposited is likely to be randomly distributed among all the vibrational modes of the molecule. Consequently, a simple statistical theory of unimolecular dissociation can be used to describe the dynamics of dissociation. Here, for the later discussion of the experimental results, we shall briefly review the theory of incoherent multiphoton excitation and the subsequent unimolecular dissociation.

We begin with a review of some basic ideas of the theory of thermal unimolecular reactions /A.13/. The reaction scheme used in the well-known RRKM theory is

\[
\begin{align*}
\delta k_1(E^* + E^* + \delta E^*) & \quad A + M \xrightarrow{k_2} A^*(E^*) + M \\
A^*(E^*) & \xrightarrow{k_d(E^*) + k^+} A^+ \rightarrow \text{products.}
\end{align*}
\] (A.1)

The reactant molecules A are energized and deenergized by collisions to and from the energy range between \(E^*\) and \(E^* + \delta E^*\) with the rate constants \(\delta k_1\) and \(k_2\) respectively. The energized molecules \(A^*\) are
converted to activated complexes $A^+$ with a rate constant $k_a$. The activated complexes subsequently dissociate with a rate constant $k^+$. Assuming the processes of activation and deactivation to be essentially single-step processes (the so-called strong collision assumption), the quantity $\delta k_1/k_2$ may be equated to the equilibrium Boltzmann distribution of molecules in the given energy range:

$$\frac{\delta k_1(E^* \rightarrow E^* + \delta E^*)}{k_2} = \frac{N^*(E^*) e^{-E^*/kT}}{Q_2} \delta E^*$$

where $N^*(E^*)$ is the density of quantum states at energy $E^*$ and $Q_2$ is the molecular partition function for all the active modes of $A$. Since relatively large amounts of energy are generally transferred in molecular collisions of highly excited polyatomic molecules (5 kcal/mole or more) and since the average excitation energies in thermal reactions are typically 5-15 kcal/mole above the critical energy $E_0$, the strong collision assumption is reasonably good for most thermal reactions. The "equilibrium hypothesis," which assumes that the steady-state concentration of activated complexes $A^+$ is equal to the equilibrium concentration which would be present if no reaction were occurring, is really implicit in the strong collision assumption.

The second major assumption of the RRKM theory is the energy randomization hypothesis, which states that the excitation energy in the active vibrational and rotational degrees of freedom is subject to rapid statistical redistribution. With this assumption, the rate of formation of the "critical configuration" (or activated complex) from the energized molecules, $k_a(E^*)$, is just proportional to the ratio
of the sum of all vibrational and rotational quantum states available to the critical configuration with vibrational-rotational energy in the range from \( E^+ = 0 \) to \( E^* - E_0 \) to the density of quantum states in the energized molecule at energy \( E^* \):

\[
\sum_{E^+ = 0}^{E^* - E_0} N^+(E^+) \Delta E^+ = \frac{k_a(E^*)}{N^*(E^*)} \tag{A.3}
\]

This is the quantum mechanical equivalent of taking the ratio of the volumes in phase space corresponding to the critical configuration and the energized molecule, respectively. The energized molecules \( A^*(E^*) \) will then dissociate in time with a probability distribution of the form

\[
p(t) \propto e^{-t/\tau^*} \tag{A.4}
\]

where \( \tau^*(E^*) = 1/k_a(E^*) \) represents an "average" dissociation lifetime.

The rate of formation of activated complexes with translational energy in the reaction coordinate between \( E_t \) and \( E_t + \Delta E_t \) is

\[
k_a(E^*, E_t) \propto \frac{N^+(E^+ = E^* - E_0 - E_t) \Delta E_t}{N^*(E^*)} \tag{A.5}
\]

This expression can be used to correctly describe the translational energy distribution of the dissociation products in the center-of-mass coordinates only if there are no interactions between the fragments after the critical configuration is passed. When this condition is met for a moderately large polyatomic molecule without excessive angular
momentum, the translational energy distribution is expected to peak near zero and fall off roughly exponentially, leaving most of the excess energy in the internal degrees of freedom of the products.

In the high-pressure limit, the rate constant of thermal unimolecular dissociation can be approximated by

\[ k_\infty = -\frac{1}{[A]} \frac{d[A]}{dt} = \int_{E^*=E_0}^{\infty} k_a(E^*) \frac{\delta k_1(E^* + E^* + \delta E^*)}{k_2} \]  

(A.6)

which reduces to the well-known Arrhenius form

\[ k_\infty = A e^{-E_0/kT} \]  

(A.7)

The Arrhenius-type dependence of the high-pressure rate constant is simply a consequence of averaging the microscopic rate constant \( k_a(E^*) \) over an equilibrium Boltzmann distribution of energized molecules with \( E^* > E_0 \).

The two basic assumptions of RRKM theory mentioned above are quite different in nature. The energy randomization hypothesis is directed toward single isolated molecules and permits calculation of the microscopic rate constant \( k_a \) as a function of excess energy in the molecule. It assumes that the intramolecular dynamics is ergodic on the time-scale of the dissociation process so that statistical considerations alone can predict the dissociation lifetimes and product energy distributions. On the other hand, the strong collision assumption is related to the special case of thermal energization and deenergization of molecules by molecular collisions. It leads to a Boltzmann distribution
of energized molecules above the critical energy and predicts an Arrhenius dependence of the rate constant on temperature at high pressure.

In MPD experiments, the absorption and the stimulated emission of infrared photons replaces molecular collisions as the means of excitation and deexcitation. Molecules which are translationally cold but vibrationally very hot are prepared. In some ways the multiphoton excitation (MPE) process resembles chemical activation where highly vibrationally excited molecules or radicals are prepared by a bimolecular addition reaction of atoms or radicals. In both cases a non-equilibrium situation is produced in which molecules can acquire internal energies well above the average thermal energy. MPE and chemical activation also differ in several important respects /A.15/. The energy distribution of chemically activated molecules is usually very narrow, most of the excited molecules having energies within 10% (or less) of the average. Also, because of the extremely rapid energy deposition which occurs in a chemical activation experiment, molecules with dissociation lifetimes in the sub-picosecond range may often be studied. In MPE, the energy distribution of the excited molecules depends on the size of the molecule, the magnitude of the critical energy, and the laser pulse conditions. The molecule continues to absorb IR photons until it reaches levels where the dissociation rate becomes comparable to or larger than the up-pumping rate due to the laser field. As will be seen later, for the typical CO₂ TEA laser with 50-100 ns pulse duration, $10^6 - 10^8$ W/cm² intensity, and reasonable absorption cross-sections of $\sim 10^{-20}$ cm², the average dissociation lifetime should fall in the 1-50 ns range, independent of the
nature of the molecule or the type of dissociation process occurring. This places most MPD experiments on a much slower timescale than the intramolecular relaxation time of highly excited polyatomic molecules, $10^{-11} - 10^{-12}$ s, derived from a series of chemical activation experiments /A.16/. This also implies the applicability of a statistical theory in describing the dissociation of multiphoton excited molecules.

In the multiphoton excitation, the width of the energy distribution is often fairly broad because of the stochastic nature of the excitation process. The distribution of molecules above the dissociation energy level also depends on how rapidly the dissociation rate constant increases with increased excitation. The RRKM theory predicts that the rate constant for large molecules with a high density of states near the dissociation level will increase rather slowly with excitation, leading to a distribution of molecules over a broad range of levels from which dissociation can occur. For small molecules and molecules with low dissociation energies, the rate constant increases more rapidly with excitation energy and then the molecules can only be excited into a narrow range of levels just above the dissociation level. The RRKM rate constants for CF$_3$I and SF$_6$ are shown in Fig. A.1. If levels with lifetimes between 1 and 10 ns contribute to the dissociation yield, the spread in excess energy is around 3 kcal/mole for CF$_3$I and 10 kcal/mole for SF$_6$.

In order to get a more quantitative picture of the population distribution of excited molecules during and after the laser pulse, some assumptions must be made concerning the dynamics of the MPE process. The simplest assumption is that the laser excitation is equivalent
to thermal heating and that the thermal population distribution is not appreciably perturbed by dissociation. This is equivalent to making the strong collision assumption in thermal unimolecular reaction theory. Then, the population distribution at any time will be a Boltzmann distribution whose temperature is determined by the average number of photons absorbed per molecule. This approach has been used by the Harvard group to interpret their measurements of the dissociation yield and the average vibrational excitation of SF₆ as a function of laser energy fluence /A.14/.

A somewhat more sophisticated model utilizes a set of phenomenological rate equations to describe the multiphoton excitation /A.17,18/. Such a model has also been considered by Lyman /A.19/. In our model we assume that: (1) The multiphoton excitation of a molecule may be described by step-wise incoherent one-photon transitions among a set of equally spaced levels in the quasi-continuum. (2) The degeneracy of each level is given by the corresponding molecular density of states. (3) The ratio of the emission and absorption cross sections for transitions between two adjacent levels is given by the ratio of the level degeneracies. (Spontaneous emission is neglected.) (4) The dissociation rates of molecules from levels above the dissociation threshold are given by RRKM theory. With these assumptions the rate equations may be written as

$$\frac{dN_m}{dt} = \frac{I(t)}{hv} \left[ \sigma_{m-1} N_{m-1} + \frac{g_m}{g_{m+1}} \sigma_m N_{m+1} - \left( \frac{g^{-1}_m \sigma_m + \sigma_{m-1}}{g_m} \right) N_m \right] - k_m N_m$$

(A.8)
where $N_m$ is the normalized population in level $m$ with energy $m\hbar \nu$,

$I(t)$ is the laser intensity, $g_m$ is the density of states of level $m$,

$\sigma_m$ is the cross section for absorption from level $m$ to $(m+1)$, and

$k_m = k_a(E^* = m\hbar \nu)$ is the RRKM dissociation rate constant for level $m$.

With given $I(t)$, $g_m$, $\sigma_m$, and $k_m$, the population distribution $N_m$ as a function of time can be calculated from Eq. (A.8).

The density of states, $g_m$, is calculated with the Whitten-Rabinovitch approximation /A.13/. Use of this approximation tacitly assumes that the molecules in the quasi-continuum are randomly distributed over all the vibrational states at a given energy. It is not obvious whether the rotational degrees of freedom should be included in the calculation of the density of states. This was investigated for SF$_6$ by calculating the density of states with the rovibrational Whitten-Rabinovitch approximation /A.18/. The ratio of density of states for adjacent levels changed by about 4% at the bottom of the quasi-continuum ($m = 3,4$) and by only 1% around the dissociation threshold. These changes cause at most a 1% difference in the population of any level. Thus, the question of the inclusion of the rotational degrees of freedom in the calculation of the density of states is not an important consideration in the rate equation model.

The absorption cross section and its dependence on excitation energy are difficult to estimate from an ab initio calculation. The lineshape of the $\nu_3$ transition of SF$_6$ has been observed to broaden and shift with increasing temperature. Thus, at the peak of the linear absorption spectrum, the absorption cross section should decrease with excitation, as has been observed by NOWAK and LYMAN /A.20/ and
In our numerical calculations on SF$_6$ the absorption cross section is assumed to have the form

\[ \sigma_m = \sigma_0 e^{-\gamma m} \]  

(A.9)

where \( \sigma_0 = 8 \times 10^{-19} \text{ cm}^2 \) and \( \gamma = 5 \times 10^{-2} \). These parameters were chosen to fit the experimental results of BLACK et al. /A.14/, as will be discussed later. A comparison of the laser-excited population distribution and a thermal distribution is shown in Fig. A.2. The laser-excited distribution with \( \langle n \rangle = 20 \) was obtained from our model calculation for a 20 ns 200 MW/cm$^2$ rectangular laser pulse. The thermal distribution with \( T = 2200 \text{ K} \) has an average excitation energy of \( \langle n \rangle h\nu \approx 20 h\nu \).

We notice that the thermal distribution is broader and has a long high-energy tail. This tail is absent in the distribution obtained from the model calculation which properly takes into account the depletion of population due to dissociation. The fact that the laser-excited distribution is narrower than the thermal distribution follows from the assumption that the absorption cross section decreases with excitation.

A more realistic model calculation should include the intensity-dependent 3-6 photon excitation over the discrete levels of SF$_6$. The existence of an intensity-dependent "bottleneck" in the excitation into the quasicontinuum was originally suggested by AMBARTZUMIAN et al. /A.22/ and subsequently shown experimentally /A.14,23/. Detailed quantum mechanical models of the discrete levels have been developed /A.22-26/ which include the rotational substructure in the vibrational levels. The time development of the excited SF$_6$ population in the
discrete levels has been calculated using such models /A.27-29/.
However, these models are too complex for our simple model calculation,
and we have used a much simpler phenomenological approach to describe
the bottleneck effect.

We assume that the quasi-continuum begins at an energy of \( 4 \hbar v \).
The excitation of population into the quasi-continuum requires different
laser intensities for different rotational-vibrational states. If
a single four-photon process is effective in exciting the population
into the quasi-continuum, then the net excitation rate is proportional
to \( I^4 \). We then have

\[
\frac{dN_{o,J}}{dt} = -a_J I^4 N_{o,J}
\]  \hspace{1cm} (A.10)

\[
N_{o,J}(t) = N_{o,J}(0) \left[\exp \left(-a_J \int_0^t I^4(t')dt'\right)\right]
\]  \hspace{1cm} (A.11)

where \( a_J \) is a constant different for each rotational substate and \( N_{o,J} \)
is the population in the \( J^{th} \) rotational state of the ground vibrational
level. The rate at which the population is coupled into the quasi-
continuum is then equal to \(-d(\sum J N_{o,J}(t))/dt\). Once in the quasi-continuum,
the population evolves according to Eq. (A.8). For a bell-shaped
laser pulse, the function \( N_{o,J}(t) \) is close to a step function and
may be approximated by

\[
N_{o,J}(t) = N_{o,J}(0) \quad \text{as long as} \quad I(t) < I_J
\]
\[
= 0 \quad \text{after} \quad I(t) \text{ has reached} \quad I_J
\]

where \( I_J \) is the coupling intensity for the \( J^{th} \) rotational state.
It is known from two-frequency experiments /A.30,31/ that the coupling intensities vary from less than 0.1 MW/cm\(^2\) to 100 MW/cm\(^2\), depending on J. For a bell-shaped laser excitation pulse, the rate of switching the population into the quasi-continuum therefore depends on time. In our calculation, we simply assume it takes the form

\[- \frac{d}{dt} \left( \sum_{J} N_{0,J} \right) = \frac{1}{2} \frac{d}{dt} \left[ \text{erf} \left( \alpha \ln \frac{I_{\text{max}}(t)}{\beta} \right) \right], \tag{A.12}\]

This should be included as an additional term in the rate equation for the bottom level of the quasi-continuum in Eq. (A.8). \(I_{\text{max}}(t)\) is the maximum intensity achieved by the laser pulse as of time t and \(\alpha\) and \(\beta\) are adjustable parameters. For a bell-shaped laser pulse, \(I_{\text{max}}(t)\) increases monotonically from zero to its maximum value and then "freezes." \(\beta\) is the intensity at which 50% of the total population is coupled to the quasi-continuum, and \(\alpha\) is a parameter which reflects the spread in the coupling intensities of the initial rotational states.

As shown in Fig. A.3, our calculation using Eq. (A.8) with Eq. (A.12) included reproduces the experimental curves of BLACK et al. /A.14/ on the absorption of photons by SF\(_6\) obtained with three different laser pulses. The parameters used in the calculation were, for the absorption cross section, \(\sigma_0 = 8 \times 10^{-19} \text{ cm}^2\), \(\gamma = 5 \times 10^{-2}\), and for the bottleneck, \(\alpha = 0.5\), \(\beta = 16 \text{ MW/cm}^2\). In the case of the 0.6 ns laser pulse, the calculation is not at all sensitive to the values of \(\alpha\) and \(\beta\) since the peak intensity is much larger than \(\beta\). For the 60 ns laser pulses, the discrete-state bottleneck has a substantial effect. It is more severe with the single-mode pulses since the peak
intensity of a single-mode pulse is less than half that of a multimode pulse. That the model calculation fits the experimental 60 ns pulse results indicates that our treatment of the bottleneck is a fair approximation.

In order to investigate the effect of the bottleneck on the population distribution, the calculation was run with 15 ns and 60 ns laser pulses each at the same energy fluence of 0.3 J/cm² (well below the threshold for dissociation). The results are shown in Fig. A.4. For the 15 ns pulse, 70% of the population is pumped into the quasi-continuum, while for the 60 ns pulse only 40% of the molecules overcome the bottleneck. However, the excited population distributions have essentially the same shape and width. While the peak intensity determines the total population in the quasi-continuum, it appears that the energy fluence essentially determines the population distribution within the quasi-continuum. Thus, the results shown in Fig. A.2 are essentially unchanged when a realistic pulse shape is used and the bottleneck effect is included.

Our calculation also answers the question of how the laser intensity affects the distribution of excess energies with which SF₆ dissociates. Figure A.5 shows the distributions which result from 60 ns and 0.6 ns laser pulses, each at an energy fluence of 7.5 J/cm². The histograms represent the total dissociation yield from each level, both during and after the laser pulse. (The fraction of dissociation which is completed during the laser pulse is 50% for the 60 ns pulse and 34% for the 0.6 ns pulse.) It is seen that the average excess energy is higher for the short pulse, since the level of excitation is determined
by the balance of up-excitation and dissociation, and the up-excitation rate is much greater in this case. This should be true whenever the energy fluence is high enough to saturate the dissociation yield, that is, when there is enough energy in the pulse to pump most of the molecules all the way up through the quasi-continuum. At sufficiently low fluences, only a small number of molecules at the high energy end of the population distribution can dissociate and most of the dissociation will occur from low-lying levels with long lifetimes. Thus, at energy fluences well below saturation, both the dissociation yield and the average level of excitation will depend on energy fluence and not much on the intensity.

The preceding general theoretical considerations on MPE and MPD are quite realistic. The experimental results obtained in molecular beam experiments which will be described in the following sections are in good agreement with the above description.
A.3. EXPERIMENTAL ARRANGEMENT

In order to understand the dynamics of infrared multiphoton dissociation of polyatomic molecules, it is necessary to carry out experiments under collision free conditions and obtain some information which is directly related to the dissociation dynamics. The positive identification of primary dissociation products, the measurement of the energy distribution of the fragments and the determination of the lifetime of the excited molecules are important data that need to be obtained in order to make an assessment of the extent of energy randomization and the level of excitation prior to the dissociation of excited molecules.

The crossed laser-molecular beam arrangement is most suited for this purpose and is used in our experimental investigations. The molecular beam apparatus used is shown schematically in Fig. A.6. The molecular beam was formed by expansion of the pure gas or a gaseous mixture using a rare gas as carrier at ~75-200 Torr stagnation pressure from a 0.1 mm-diameter quartz nozzle. Three stages of differential pumping were used along with two conical skimmers and a final collimating slit to produce a well defined beam ~2 mm in diameter in the laser irradiation region. The molecular beam had a very sharply delineated angular distribution of 1.2° full width at half-maximum (FWHM). Three stages of differential pumping were found to be necessary for this type of experiment in order to be able to detect the dissociation products near the molecular beam, since the fragmentation of beam molecules in the ionizer of a mass spectrometer produces the same mass peaks as those from the dissociation products. The velocity
distribution of the molecular beam typically had a FWHM spread of 25% of the average velocity, or better. The density of molecules in the beam in the irradiation region was $\sim 3 \times 10^{11}$/cm$^3$. The velocity spread and the number density of the molecular beam are both limited by the stagnation pressure which had to be kept low to avoid the formation of Van der Waals dimers and polymers during the expansion. A Tachisto TAC II grating tuned CO$_2$ TEA laser ($\sim 1.0$ J/pulse) was used in our experiments as the excitation source. The laser beam was admitted into the vacuum chamber via a ZnSe lens with a 25.4-cm focal length. The power and the energy fluence of the laser at the molecular beam was adjusted by varying the distance between the focal region of the lens and the molecular beam. The fragments produced by multiphoton dissociation of polyatomic molecules at the small intersection region were detected by a triply differentially pumped quadrupole mass spectrometer utilizing electron bombardment ionization and ion counting. The pressures in the three regions of the detector were maintained at $\sim 10^{-9}$, $\sim 10^{-10}$ and $\sim 10^{-11}$ Torr by a combination of ion pumps, a sublimation pump, a liquid nitrogen trap and a liquid helium cryopump. The partial pressure of the beam molecule in the third region where the ionizer is located was usually kept below $10^{-13}$ Torr. The angular position of the mass spectrometer around the beam intersection point could be varied so that the angular distribution of the fragments could be measured. The mass filter was usually adjusted to provide better than unit mass resolution. As shown schematically in Fig. A.7, external triggering at 0.5 Hz was used to fire the laser and to enable a dual-channel scaler for recording counts of fragments from the mass
spectrometer. Separate adjustments of delay and gate times were made to ensure that one scaler channel recorded only background (i.e., with the laser pulse off) while the other recorded both background and signal. Typically, 100-1000 laser shots were used to measure the fragments produced at each laboratory angle \( \theta \) (see Fig. A.6) for the measurements of angular distributions. The angular resolution of the detector was 1°. In order to positively identify the dissociation products and to check for possible secondary dissociation of a primary product by the same laser pulse, the angular and velocity distributions were scanned at several mass peaks in the mass spectra of the dissociation products of a molecule under investigation. The fragment velocity distributions at various laboratory scattering angles were obtained by determining the arrival time of each fragment, after a flight path of 21 cm, at the detector, relative to the time origin defined by the laser pulse. This was done by multiscaling the mass spectrometer output signal. Typically, a 10 s channel width was used in a scan over 2.5 ms.

The dissociation products and their angular and velocity distributions were extensively measured while varying the laser frequency, power and energy fluence and the vibrational and rotational temperatures of the molecules.
A.4 EXPERIMENTAL RESULTS

The major MPD products identified in our molecular beam experiments are listed in the first column of Table A.1, which summarizes our results. The dissociation products observed are typically those from the channel with the lowest activation energy. According to the measurements by several other groups /A.7-12/ using laser induced fluorescence detection, they appear in their ground electronic states, or in some cases /A.32-33/, in low-lying electronic states.

For C₂F₅Cl and CHClCF₂, two dissociation channels corresponding to the two lowest activation energies have been observed. For CH₃CF₂Cl the HF and HCl molecular eliminations were suggested to have, within experimental uncertainty, the same activation energies in earlier thermal dissociation studies, but the HCl elimination is the only channel observed in our experiments. For SF₆ and CFCl₃, secondary dissociation of the primary products is observed at high energy fluence (SF₅ → SF₄ + F, CFCl₂ → CFCI + Cl).

In the cases where two competitive dissociation channels are observed, the intensity of the laser pulse was found to influence the branching ratio. Figure A.8 shows the relative dissociation yield of C₂F₅Cl into CF₃ + CF₂Cl and C₂F₅ + Cl as a function of laser energy. The chlorine atom elimination has a threshold at 0.5 J/cm² and saturates at 1 J/cm². The channel producing CF₃ + CF₂Cl has approximately the same threshold, but as the intensity is increased, the fraction dissociating by C-C bond rupture continues to increase.
The laboratory angular and velocity distributions for SF₅ in the fluorine atom elimination from SF₆ are shown in Figs. A.9 and A.10. The angular distribution of the SF₅ peaks as close to the SF₆ beam as can be measured (5°) and falls off monotonically with increasing angle. The velocity distributions of SF₅ shown in Fig. A.10 were obtained from the time of flight measurements at three angles. Also shown is the SF₅ beam velocity distribution. The angular and velocity distributions for SF₆ are typical of the other halogen atom elimination reactions. For example, Figs. A.11-13 show the laboratory angular and velocity distributions of CF₃ and I from MPD of CF₃I.

Translational energy distributions of dissociation products are derived from the measured laboratory angular and velocity distributions. First, an assumed center-of-mass translational energy distribution of the fragments is transformed to the laboratory coordinates, including the convolution over the beam velocity distribution and the length of the ionizer in the mass spectrometer. Then, the angular and velocity distributions in the laboratory coordinates can be calculated and fit to the experimental curves. Center-of-mass angular distributions of products are found to be isotropic for all systems studied. This can be concluded from the agreement between experiments and theoretical curves deduced using this assumption, and from the observation that our results were independent of laser polarization. Figure A.14 shows the translational energy distribution of SF₅ + F derived from the experimental results. The curves drawn in Figs. A.9 and A.10 are the angular and velocity distributions calculated from the translational energy distributions shown in Fig. A.14.
Columns 4 and 5 of Table A.1 give information on the average translational energy and the peak of the translational energy distribution. It is clearly seen that except for some 3- and 4-center eliminations, which are known to have additional potential energy barriers for dissociation, the translational energy distributions all peak at zero kinetic energy and the average translational energies of the products are generally very low.

The systems with an additional potential energy barrier in the exit channel have characteristically different translational energy distributions, which are reflected in laboratory angular and velocity distributions. Three center elimination of HCl from CHF₂Cl is one of the examples. The velocity distributions of the HCl in this case is shown in Fig. A.15. The center of mass translational energy distribution peaks at 5 kcal/mole and the average translation energy is as high as 8 kcal/mole, as shown in Fig. A.16. Four center elimination of HCl from CH₃CCl₃ and CH₃CF₂Cl and C-C bond rupture in C₂F₅Cl all have similar characteristic translational energy distributions.
A.5. DISCUSSION

As already discussed in the theory section, a simple picture can be used to describe MPD: the incoherent stepwise multiphoton process excites the molecules through the quasi-continuum to and beyond the dissociation energy level. The level of excitation is eventually limited by molecular dissociation, which can be accurately described by the statistical theory (RRKM theory) of unimolecular reactions. The results from our molecular beam experiments have provided sufficiently detailed information on important features of the MPD process for drawing such a picture. In the following discussion we will emphasize the collisionless aspects of the process, and only briefly mention a few of the additional effects that have to be taken into account if collisions cannot be neglected.

Let us start by looking at some of our typical experimental results on the translational energy distribution of the dissociation fragments. Shown in Fig. A.10 are the velocity distributions of SF₅ fragments from MPD of SF₆ at various angles with respect to the SF₆ beam /A.18,34/. We see that they are only slightly broader than that of the primary SF₆ beam because the average translational energy imparted to the fragments in the dissociation is quite small. The same conclusion can be drawn from the angular distribution of SF₅ fragments shown in Fig. A.9; it falls off rapidly as the angle from the SF₆ beam increases, again indicating that very little translational energy is released to the fragments. More quantitatively, this can be seen from the translational energy distribution of the fragments as shown in Fig. A.14, where the distribution curves actually yield velocity and
angular distributions which fit the measured ones in Figs. A.9 and A.10 very well.

This form of translational energy distribution of the fragments is actually predicted by the RRKM theory. As explained in the theory section, it predicts that as the excitation in a molecule increases above the dissociation energy, the dissociation rate constant increases. This will tend to favor dissociation through the lowest-energy dissociation channel. Experiments, in particular those using the molecular beam, have shown that the MPD of most molecules proceeds through the lowest-energy channel /A.6,34-36/. The RRKM theory also predicts how the excess energy (excitation energy minus dissociation energy) is distributed among the various vibrational modes of the molecule in the critical configuration, including the relative motion of the dissociating fragments. Fig. A.14 shows the translational energy distributions that were used to fit the experimental results, calculated from the RRKM theory for excess energies of 5, 8 and 12 CO₂ laser photons. The good fit indicates that the RRKM theory describes MPD quite well.

The MPD results on halogenated methanes show (see Table A.1) that most of the molecules dissociate with excess energies of 1-3 CO₂ laser photons, as compared to around 8 photons for SF₆. On the other hand, C₂F₅Cl dissociates with around 13 photons of excess energy. How can the average excess energy depend so much on molecular structure?

To understand the above results we should consider the laser excitation scheme presented in the theory section and in Fig. A.17. The laser excites the molecule up the ladder of energy levels with
a net up-excitation rate proportional to the laser intensity. As
the excitation increases above the dissociation level the dissociation
rate increases rapidly, and soon starts to compete with the up-excitation.
The average level of up-excitation from which most of the molecules
will dissociate is then determined by a balance between dissociation
and up-excitation. By using this simple picture of competition between
dissociation and up-excitation, we can draw a number of important conclu-
sions.

1) In a heavier, more complex molecule that has more degrees
of freedom and more low frequency vibrations, (e.g., SF$_6$ or C$_2$F$_5$Cl),
the dissociation rate constant should increase more slowly with increase
in energy. This was quite dramatically displayed in Fig. A.1. Conse-
quently, the heavier molecules tend to reach higher levels of excitation
before they dissociate. This explains why the C$_2$F$_5$Cl molecule has
a higher excess energy than SF$_6$, which in turn has more excess energy
than the halogenated methanes.

2) If the laser pulse is very short, none of the molecules dissociate
before the laser pulse is over. Then the population distribution and
the level of excitation from which dissociation occurs is completely
determined by the total pulse energy fluence. However, if the laser
pulse is sufficiently long, the excitation level reached is limited
by the dissociation, and at this level the up-excitation rate and
the dissociation rates are about equal. Thus the level of excitation
in this case should be higher with higher intensity, or at laser frequencies
where the transition rates are higher.
When the dissociation yield is near saturation, the time it takes for a molecule to be pumped up above the dissociation energy is about equal to the pulse duration. The time it takes to make a transition above the dissociation energy is a reasonable fraction of this time (say 1/10-1/50, since it takes some 10-50 transitions to get above the dissociation energy). Thus, in the case of dissociation rate limited excitation, the lifetime corresponding to the average level of excitation is of the order of 1/10 of the laser pulse duration. Our molecular beam experiments were done with a laser pulse of about 60 ns FWHM. From Table A.1 we see that the dissociation lifetimes corresponding to the level of excitation calculated from the RRKM theory to fit the observed translational energy distributions are indeed in the 1-100 ns range (mostly around 10 ns).

3) The RRKM dissociation rate constant should increase more rapidly with excess energy if the dissociation energy is lowered. CF$_3$I has a dissociation energy slightly more than half of that of SF$_6$, and this accounts in part for the difference in their dissociation rate constants shown in Fig. A.1. An even clearer example is N$_2$F$_4$, which has a dissociation energy of only about half that of CF$_3$I. Even though it has one atom more than CF$_3$I, its dissociation rate grows so rapidly with excess energy that dissociation already dominates over up-excitation at a level one CO$_2$ laser photon above the dissociation energy. This is shown quite clearly by the translational energy distribution of NF$_2$ fragments in Fig. A.18, as there are no fragments with more than one photon or 3 kcal/mole of translational energy.
4) Since only a small fraction of the excess energy is released as translational energy, most of the excess energy should then remain as internal energy in the fragments. For heavy, complex molecules which reach high levels of excitation before dissociating, the fragments emerging from dissociation are already excited to their quasi-continuum and can readily absorb more energy from the laser field to go through another MPD process. This process of secondary dissociation is of course more likely to occur if the fragments have a strong absorption band coinciding with the laser frequency. In our experiments, we have observed secondary dissociation in SF$_6$ and CFCl$_3$, with the fragments SF$_5$ and CFCl$_2$ dissociating further to form SF$_4$ and CFCl, respectively. The various products were identified through their different electron impact ionization spectra in the mass spectrometer. The laser frequency used was not in near resonance with any known strong IR absorption lines of CFCl$_2$ or SF$_5$, so the observed secondary dissociation must result from excitation of SF$_5$ and CFCl$_2$ already in the quasi-continuum. Of course, for this to make sense, the primary dissociation must take place before the laser pulse is over. This is certainly the case - the translational energy distributions of SF$_5$ and CFCl$_2$ indicate that they are produced from parent molecules with lifetimes of around 10 ns, compared to the laser pulse duration of more than 60 ns.

In MPD of CF$_3$Cl, CF$_3$Br and CF$_3$I, the CF$_3$ fragment produced has little internal energy (1-2 CO$_2$ laser photons), but CF$_3$ in the ground states is known to absorb close to the laser frequency used. Although the molecular beam experiments were not sensitive enough to detect dissociation of CF$_3$, in gas cell experiments on the same three molecules
CF₂ radicals and F atoms have been observed, indicating that a secondary dissociation of CF₃ may have taken place.

Many of the products observed by the extremely sensitive laser induced fluorescence detection method are probably also produced from sequential dissociations of intermediate products. For example, C₂, CN and CH have been observed /A.10-12,33/ in the dissociation of molecules with six or more atoms. Unfortunately, the laser induced fluorescence detection methods is not able to reveal anything about the intermediate steps leading to these small final products. It seems that the secondary or sequential dissociation is an unavoidable effect in the MPD at high energy fluence of all but the lightest, simplest molecules. This is a factor which often complicates the studies of the MPD process, regardless of the method used for detection and analysis of the dissociation products.

5) For the heavier, more complex molecules, competing dissociation channels may also open up, provided their dissociation energies are not too far above that of the lowest energy channel. If the laser intensity is sufficiently high, the molecule can be excited well above the dissociation energies of several channels before dissociation dominates over up-excitation. Then several dissociation channels may start to compete with the lowest one. We should stress here that this effect is actually expected from the statistical theory of unimolecular dissociation. A system in which such an effect has been observed is C₂F₅Cl. The energetics of the various dissociation pathways are not well known, except for the lowest one, which is the Cl atom elimination, with a dissociation energy of about 83 kcal/mole.
The next lowest channel is probably C-C bond rupture, with a dissociation energy of around 97 kcal/mole. The RRKM calculations indicate that the rate constant for the C-C bond rupture grows more rapidly with excess energy than that for the Cl atom elimination. As we have already seen, the average level of excitation in C$_2$F$_5$Cl pumped by a 1-J TEA laser can be around 13 CO$_2$ laser photons (40 kcal/mole) above the C-Cl bond energy, well above the dissociation energy of the C-C bond rupture so that the C-C dissociation rate can be comparable to the C-Cl dissociation rate. In the experiments, a competition between the two channels has actually been observed. If we look at low laser intensities, the Cl atom elimination dominates over the C-C bond rupture. As the laser intensity is increased, thus pumping the molecules to higher levels of excitation, the Cl elimination channel very rapidly saturates, whereas the C-C bond rupture becomes increasingly important. This effect is not peculiar to MPD experiments. In pyrolysis of ethane compounds it has long been observed that at low temperature, atomic elimination reactions dominate the dissociation, but as the temperature is increased, C-C bond rupture becomes progressively more important, making the analysis of such reactions exceedingly complicated.

Now, many of the results discussed under 1)-5) above have also been obtained in an explicit model calculation on SF$_6$, using the simple set of rate equations presented in the theory section /A.17-19/. By fitting the free parameters in the model to experimental results on energy absorbed as a function of input laser energy fluence and laser pulse duration, we can predict the dissociation yield as a function of energy fluences, the onset of secondary dissociation, the level
of excitation from which dissociation occurs, and thus, the translational energy distribution in the fragments. As explained in the theory section and shown in Figs. A.3 and A.5 all the results agree with the experiments, and illustrate quite clearly in a more quantitative way what we have discussed above in qualitative terms.

How will these results be modified if we cannot neglect molecular collisions? Depending on the collision partners, we can have a number of complications:

1) Collisions between excited molecules will lead to a thermalization of the energy deposited by the laser in the molecules via intermolecular vibrational energy transfer. Thus any differences between thermal heating and multiphoton excitation will be washed out. The isotopic selectivity of the process will decrease, due to energy transfer between different isotopic species. Rotational and vibrational intermolecular energy transfer during the laser pulse can increase the number of molecules interacting resonantly with the laser field, thus reducing the bottleneck for excitation out of the discrete levels into the quasi-continuum. Collisionally induced dissociation can also occur, even in the absence of multiphoton dissociation.

2) Collisions between excited molecules and cold molecules will lead to a deactivation of the excited molecules. The cold collision partners may be buffer gases, if present, or reaction products from the dissociation. Their presence will increase the energy absorption necessary for a given dissociation
yield, and lower the level of excitation. Thus, in cases with competing dissociation channels, the lowest energy channel will be favored. Since the excited products from the dissociation can also be deactivated via collisions, secondary dissociation of the products will be inhibited.

3) Collisions between dissociation products, and between products and other atoms or molecules present usually lead to chemical reactions. The products from MPD are mostly highly reactive free radicals. Thus recombination or disproportionation of the dissociation products may occur, and complicated chemical reaction chains may follow the primary dissociation. Analysis of the process is complicated, and dependent upon detailed information on the chemical kinetics of the reactions involved. Little information about the dynamics of the primary dissociation can be deduced from the final products.

In the preceding discussion on the translational energy distribution of fragments, we have actually only considered the simple cases where the observed distributions are in agreement with prediction of the RRKM theory. This is usually true for simple bond rupture reactions /A.36/. There is negligible interaction between the fragments once the critical configuration is passed so that the energy distribution in the fragments remains the same as in the critical configuration calculated in the RRKM theory. However, in cases where such interaction cannot be neglected, the simple RRKM theory we have used cannot take into account this interaction, and translational energy distributions very different from the ones we have discussed so far may result. For a number of
molecular elimination reactions, such as three center elimination reactions from halogenated methanes, and four center elimination from halogenated ethanes and ethenes, there is a considerable potential energy barrier between reactant and products. This potential energy will have to be distributed between the various vibrational, rotational and translational degrees of freedom in the fragments as they move away from the critical configuration on the top of the barrier. The RRKM theory cannot predict anything about how the energy will be distributed. It will depend on the nature of the potential energy surface for the fragments.

As an example, we will discuss the dissociation of CHF$_2$Cl into CF$_2$ + HCl, which has been studied in a molecular beam /A.35/ as well as with laser induced fluorescence detection of the CF$_2$ fragment /A.8/. Thus, translational, as well as rotational and vibrational energy distributions in the CF$_2$ fragment have been measured. The conclusions that can be drawn from the results on CHF$_2$Cl are representative for molecules with this kind of dissociation dynamics.

The velocity distribution of HCl fragments at 10° from the CHF$_2$Cl beam is shown in Fig. A.15, compared to the distribution calculated from the translational energy distribution in Fig. A.16. We see that the products are quite a bit faster than the CHF$_2$Cl beam, due to the considerable amount of energy gained from the dissociation. Most CF$_2$ fragments have a translational energy of more than 2 kcal/mole while only a small percentage have less than 1 kcal/mole. STEPHENSON and KING /A.8/ found the population distribution in the vibrational modes of CF$_2$ to be well represented by a thermal distribution of
temperature 1160 K. The average rotational energy was also estimated in the experiments, although its value was too high for a detailed measurement of the distribution to be made. However, assuming a thermal distribution, a rotational temperature of about twice the vibrational temperature was obtained. The high translational energy content in the fragments means that there is a strong repulsive interaction between the departing fragments after they pass through the critical configuration. This repulsive interaction is quite asymmetric, giving the fragments considerable rotational energy.

However, we want to emphasize that although RRKM theory alone may be inadequate for predicting the final energy partitioning in the fragments, it still predicts the dissociation rates. If we add up all the energies in the fragments in the HCl elimination from CHF₂Cl, using the results of King and Stephenson, we get to a level of excitation corresponding to an RRKM lifetime around 1 ns. This is what we should expect from the statistical theory of MPD as in the cases of the other halomethanes. In fact, there exists no evidence in all the cases we have studied that the general statistical picture of the multiphoton excitation and dissociation process does not apply.
A.6 CONCLUDING REMARKS

There are still a number of assumptions and theoretical predictions about the dissociation that need to be checked experimentally. The partition of energy between all degrees of freedom in at least one of the two fragments from the dissociation should be measured in a case where the RRKM theory predicts the distributions. The dissociation lifetimes should be measured directly and independently, together with their dependence on laser intensity, under well characterized conditions. The processes of secondary dissociation and competing dissociation channels need better characterization. The methods that so far have revealed the most about the dissociation process are the molecular beam method and the laser induced fluorescence method. A natural extension would be to use laser induced fluorescence as a detection method in a molecular beam experiment. Studies of this kind are already being prepared in several laboratories. The work is hampered by the low particle densities involved in molecular beam experiments, insufficient knowledge of the spectroscopy of many of the radicals produced in the dissociation, and lack of tunable lasers in the uv frequency ranges of interest for many compounds.

Although there are some detailed questions which still need to be further investigated, the general physical picture constructed from various experimental and theoretical investigations is quite adequate for understanding and predicting many important features of the MPD process under various conditions. But since MPD is a rather complex process, it is not possible to draw reliable conclusions unless all the factors involved are carefully analyzed. The dependence of
the dissociation yield and the dynamics of dissociation on both the laser intensity and energy fluence is an important example.

For a given chemical species, the laser intensity required for a certain fraction of the molecules to overcome the discrete state bottleneck not only depends on the frequency, but also on the vibrational and rotational temperature of the molecules. Once the molecules are excited to the quasi-continuum, the energy fluence, not the power of the laser, was shown to be responsible for driving the molecules through the quasi-continuum and beyond the dissociation level. But in most of the gas cell experiments, the dissociation yield of those molecules in the quasi-continuum is not simply related to the energy fluence alone. For molecules lying above the dissociation level, there is a complicated competition between unimolecular dissociation, collisional deactivation and laser up-excitation. Consequently, for a given gas pressure and a given laser energy fluence, a higher laser intensity should result in a higher level of excitation and an increased rate of dissociation. This in turn reduces the effect of collisional deactivation and thus increases the dissociation yield. In general, for smaller molecules, the laser intensity influences the yield by limiting the fraction of the molecules which can be excited to the quasi-continuum, but since the lifetime of small molecules becomes very short after only a couple of excess photons are deposited beyond the dissociation threshold, collisional deactivation could be overcome with a rather moderate intensity at low pressure. On the other hand, for larger molecules with many vibrational degrees of freedom, if an appropriate frequency is chosen, a large fraction of the molecules
will reach the quasi-continuum at a very moderate laser intensity. But since many more excess photons are required before the dissociation lifetime becomes comparable to the mean collision time, the laser intensity is expected to strongly influence both the dissociation yield and the ratio of competitive dissociation channels by controlling the level of excitation beyond the dissociation energy.

In most of the experiments carried out with a CO₂ TEA laser, one often adjusts the laser intensity or energy fluence by either adjusting the focusing condition or attenuating the laser output. Consequently both the laser intensity and energy fluence are often varied simultaneously. If the energy fluence requirement for dissociation is met, the intensity of the laser is already high enough to pump some of the molecules to the quasi-continuum and dissociation is observed. However, it is important to keep in mind that both the intensity and energy fluence of the laser can separately affect the experimental results. Once the complicated dependence of the excitation and dissociation dynamics on the initial distribution of molecules over vibrational and rotational states, and on the frequency, intensity, and energy fluence of the laser is properly taken into account, we are indeed in a very good position to understand and predict the general behavior of MPD of the systems of interest.

ACKNOWLEDGEMENT

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Table A.1. Dynamics of multiphoton dissociation.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Endoergicity (kcal/mole)</th>
<th>Potential energy barrier (kcal/mole)</th>
<th>Average translational energy (kcal/mole)</th>
<th>Peak of translational energy distribution (kcal/mole)</th>
<th>Estimated average energy available to products (kcal/mole)</th>
<th>Estimated lifetime (ns)</th>
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<tr>
<td>SF₅ + SF₅ + F</td>
<td>93</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>25</td>
<td>20</td>
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<tr>
<td>SF₆ + F</td>
<td>51</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>7</td>
<td>20</td>
</tr>
<tr>
<td>CF₃Cl + CF₃ + Cl</td>
<td>86</td>
<td>0</td>
<td>1.1</td>
<td>0</td>
<td>4</td>
<td>5</td>
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<td>CF₃Br + CF₃ + Br</td>
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<td>1.2</td>
<td>0</td>
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<td>2</td>
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<td>CF₃I + CF₃ + I</td>
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<td>0</td>
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<td>1</td>
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<tr>
<td>CF₂Cl₂ + CF₂Cl + Cl</td>
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<td>1.6</td>
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<td>7</td>
<td>5</td>
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<td>CFCl₃ + CFCl₂ + Cl</td>
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<td>(NH₃)₂ + 2NH₃</td>
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<td>0</td>
<td>1.5</td>
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<td>~0</td>
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<td>&gt;0</td>
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<td>~0</td>
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<td>55</td>
<td>12</td>
<td>6</td>
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REFERENCES


FIGURE CAPTIONS

Fig. A.1 RRKM dissociation rates as functions of excess energy for CF₃I and SF₆ (XBL 785-8835)

Fig. A.2 Comparison of the laser-excited SF₆ population distribution with \( \langle n \rangle = 20 \) with two thermal distributions: one with 

\[ T = 2200 \text{ K} \] corresponding to \( \langle n \rangle = 20 \) and the other with 

\[ T = 1800 \text{ K} \] obtained from the equipartition theorem 

\[ T = 20 \frac{h \nu}{15 \text{ K}} \] (XBL 777-5750A)

Fig. A.3 Results of the model calculation for the average number of photons absorbed by SF₆ vs energy fluence for three laser pulses. These results are compared with the experimental data of BLACK et al. (A.14) (XBL 792-8281)

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Experiment</th>
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<tr>
<td>0.6 ns pulse</td>
<td>.</td>
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<tr>
<td>60 ns multimode pulse</td>
<td>( \triangle )</td>
</tr>
<tr>
<td>60 ns single mode pulse</td>
<td>( \Box )</td>
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</table>

Fig. A.4 SF₆ population distribution for 15 ns (___) and 60 ns (---) laser pulses, each at an energy fluence of 0.3 J/cm². (XBL 792-8452)

Fig. A.5 Total dissociation yield of SF₆ vs the number of excess photons for 0.6 ns and 60 ns laser pulses each at an energy fluence of 7.5 J/cm². (XBL 792-8351)

Fig. A.6 Schematic of the apparatus used for the measurements of angular and velocity distributions of fragments from multiphoton dissociation of polyatomic molecules. (XBL 768-10162)
Fig. A.7 Experimental arrangement. The "SF₆ beam source" is the molecular beam source. The pulse generator triggers the laser (which partly dissociates a section of the molecular beam) and the multichannel scaler, opens a gate to scaler 1 a few hundred microseconds later (to count dissociation product signal and background signal) and a gate to scaler 2 a few milliseconds later (to count background signal only). (XBL 768-10159)

Fig. A.8 Dissociation yields for the products from MPD of C₂F₅Cl
(XBL 791-7900)

\[ \text{C}_2\text{F}_5\text{Cl} \rightarrow \text{C}_2\text{F}_5 + \text{Cl} \ (\text{C}_2\text{F}_4^+ \text{detected}) \]

\[ \text{C}_2\text{F}_5\text{Cl} \rightarrow \text{CF}_3 + \text{CF}_2\text{Cl} \ (\text{CF}_2\text{Cl}^+ \text{detected}) \]

Fig. A.9 Angular distribution of SF₅ fragments from MPD of SF₆
(XBL 785-8834A)

- - - experimental distribution
- - - RRKM theory, 5 kcal/mole excess energy
- - - RRKM theory, 8 kcal/mole excess energy
- - - RRKM theory, 12 kcal/mole excess energy

Fig. A.10 Speed distribution of SF₅ fragments from MPD of SF₆ at 5₀, 10₀, and 15₀ from the SF₆ beam. Symbols as in Fig. 10.

Bottom: SF₆ beam speed distribution (XBL 792-8359)
Fig. A.11 Angular distribution of CF₃ fragment from MPD of CF₃I.  
(XBL 783-444)  
- experimental distribution  
--- RRKM theory, 3 kcal/mole excess energy  
----- RRKM theory, 4.5 kcal/mole excess energy  
.... RRKM theory, 6 kcal/mole excess energy  

Fig. A.12 Angular distribution of I atoms from MPD of CF₃I. Symbols as in Fig. A.12 (XBL 783-442)  

Fig. A.13 Speed distribution of I atoms from MPD of CF₃I at 10°, 15°, 20° and 25° from the CF₃I beam. Symbols as in Fig. A.11. Bottom: Speed distribution of CF₃I beam (XBL 782-261)  

Fig. A.14 Center-of-mass translational energy distribution of the fragments from the MPD of SF₆, calculated from RRKM theory. Symbols as in Fig. A.9 (XBL 792-8354A)  

Fig. A.15 Speed distribution of HCl fragments from the MPD of CHF₂Cl  
(XBL 781-4439A)  
- experiment  
--- calculated from Fig. A.16  

Fig. A.16 Center-of-mass translational energy distribution in the fragments from MPD of CHF₂Cl (XBL 781-4438A)  

Fig. A.17 Schematic representation of the excitation-dissociation process around the dissociation energy.  

Fig. A.18 Center-of-mass translational energy of a pair of NF₂ fragments from the MPD of N₂F₄. (XBL 783-446A)
Fig. A.1

RATE CONSTANT ($10^{-9}$ s$^{-1}$)

EXCESS ENERGY (KCAL/MOLE)

$\text{CF}_3\text{I}$

$\text{SF}_6$
Laser Excitation

\[ <n> = 20 \]

\[ T = \frac{20h \nu}{15k} \]
\[ = 1800 \text{ K} \]

\[ T = 2200 \text{ K} \]
\[ <n> = 20 \]

Fig. A.2
Fig. A.3 XBL 792-8281
Fig. A.4.
Fig. A.5
Fig. A.6
Fig. A.7
Fig. A.9

\[ \text{SF}_6 \rightarrow \text{SF}_5 + \text{F} \]

**MPD YIELD (arb. units)**

**ANGLE OF DETECTION**
$SF_6 \rightarrow SF_5 + F$
$\text{CF}_3 \text{I} \rightarrow$

$\text{CF}_3 + \text{I}$

Fig. A.11
Fig. A.12

$CF_3I \rightarrow \ CF_3 + I$

I atom yield $Y(\theta)$ (arbitrary units)

Angle of detection $\theta$ (deg)
Fig. A.13
Fig. A.14
Fig. A.15

\[ \text{CHF}_2\text{Cl} \rightarrow \text{CF}_2 + \text{HCl} \]
Fig. A.16
Fig. A.17
Fig. A.18

\( \text{N}_2\text{F}_4 \rightarrow 2 \text{NF}_2 \)

Y-axis: Probability of energy (arbitrary units)
X-axis: Translational energy (kcal/mole)
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