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CROSSED LASER AND MOLECULAR BEAMS STUDIES OF MULTIPHOTON DISSOCIATION

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In 1973, Canadian [1] and Russian [2] groups reported the observation of visible luminescence from CO₂ laser-irradiated molecular gases (SiF₄, NH₃, C₂F₃Cl) at powers well below the breakdown threshold. The extremely fast rise-time and the pressure-dependence of one part of the luminescence suggested that the molecules might be absorbing tens of photons required for dissociation under collisionless conditions. The demonstration of isotopic selectivity in the multiphoton dissociation (MPD) of a variety of molecules [3] supports this conclusion. The alluring possibility that MPD might lead to mode-selective bond breaking in molecules has also been suggested [4].

The mechanism by which single molecules absorb up to 30 (or more) infrared photons has been the subject of numerous theoretical studies [5-8]. The simultaneous absorption of ~ 30 photons would require laser intensities near the breakdown threshold, i.e., ~ 10 GW/cm² or more. However, in SF₆, a laser intensity of only ~ 10 MW/cm² (corresponding to a pulse energy of ~ 1 J/cm²) is sufficient for MPD to occur [9]. Evidently, the absorption process must consist of a succession of near-resonant one-photon steps. A number of suggestions as to how the molecule overcomes the anharmonicity of the vibrational ladder in the stepwise resonant absorption have been offered. In the initial step (or steps) of excitation over the discrete states in the low energy region, rotational compensation of the anharmonicity is probably important. Additionally, for molecules with degenerate vibrational modes (SF₆ being a popular example), the splitting of the degeneracy of the excited vibrational levels by Coriolis coupling and anharmonic coupling with other modes can also be helpful [10]. The extent and importance of hot-band absorption in the initial excitation process has yet to be thoroughly investigated. Since the density of states of a polyatomic molecule increases very rapidly with energy, the energy levels soon form a quasicontinuum. For SF₆ at 5000 cm⁻¹ the density of states is already ~ 10³/cm⁻¹. Therefore, once the molecule makes transition over the discrete states into the quasicontinuum, the subsequent transition through the quasicontinuum and on past the dissociation limit are all "resonant". The above picture is supported by measurements of the frequency-dependence on MPD in a two-laser experiment [5,6].

Experimentally, the usual approach to studying MPD has been to irradiate a low-pressure gas medium in a sample cell with CO₂ laser pulses and analyze the gas before and after the irradiation by infrared absorption and mass spectroscopy. In some cases induced luminescence in the gas has also been monitored during the irradiation, assuming the production of electronically excited fragments is not likely [11]. Measurements have been carried out on a wide variety of gases and gas mixtures as a function of pressure, laser frequency, power, pulsewidth, etc. The major difficulty in such experiments is that the

results are always influenced by molecular collisions and chemical reactions which follow the laser excitation. It is difficult to answer questions such as: do vibrationally excited molecules react with one another; how many photons are absorbed per molecule dissociated; do the primary dissociation fragments undergo secondary dissociation in the laser field; does the method of detection actually probe the primary dissociation channel? The last question is particularly important in the light of numerous reports of MPD proceeding non-statistically, i.e., in other than the lowest dissociation channel [4,12]. Even the use of ultra-short CO₂ laser pulses [9] which are much shorter than the mean molecular collision time does not necessarily free the results from collisional effects, since the dissociation lifetime of the molecules can still be longer than the collision time. This is especially important near threshold where dissociation lifetimes are long.

By using a crossed laser and molecular beams method many of these problems may be eliminated. The collisionless nature of the process may be unambiguously established. By using a rotatable mass spectrometer direct identification of the dissociation products can be made, and angular and velocity distributions of the products can be measured, so that information regarding the excitation and dissociation dynamics can be obtained. Another advantage is that reactant purity is not as critical in a beam experiment as it is in a gas cell experiment, where even trace impurities may strongly affect the chain reactions following free radical production in MPD. Beam experiments are also free from wall effects which plague some gas cell experiments.

There are also difficulties to be overcome in the molecular beam method, however. The formation of van der Waals complexes in the supersonic beam expansion must be avoided, since the complexes will be dissociated into monomers by the laser field and the mass spectrum of the monomer may interfere with that of the dissociation fragments of the molecule. The mass spectra of the products must also be established, since if the products are highly vibrationally excited, their mass spectra may differ appreciably from tabulated spectra taken at room temperature. Additional complications arise from secondary dissociation of the primary dissociation products [13] and competing dissociation channels [14].

Experimental Arrangement

Our experimental setup is shown in Fig.1 and has been described elsewhere [13,14]. Briefly, the molecular beam was formed by expansion of the gas of interest at ~150 torr stagnation pressure from a 0.1 mm diameter quartz nozzle, producing a molecular density in the beam of $\sim 3 \times 10^{11} \text{ cm}^{-3}$. A Tachisto CO₂ TEA laser with ~1 J/pulse was focused by a 25 cm focal length ZnSe lens. The two beams crossed at the collision center and the dissociation fragments were analyzed by a rotatable detector consisting of an ionizer, quadrupole mass spectrometer, and a gated counting system. Angular resolution better than $\pm 0.5^\circ$ was achieved. Velocity distributions of the fragments were measured with a 256-channel scaler which was gated by the laser pulse.

Experimental Results and Discussion

In the past two years we have studied MPD of a variety of molecules including SF₆, N₂F₄, and numerous halogenated methanes, ethanes, and ethylenes. What follows is a brief discussion of some of the results and the general conclusions we have drawn about MPD.

Fig.1 Schematic of the apparatus used for crossed laser and molecular beams studies of MPD. The beam is triply differentially pumped allowing pressures of $\sim 10^{-7}$ torr in the fragmentation region

A. Simple Bond Dissociation Reactions

The first molecule studied by the crossed laser and molecular beams method was SF_6 [13,15]. At low laser energy density ($< 10 \text{ J/cm}^2$) the dissociation products were almost exclusively $\text{SF}_5 + \text{F}$, which is the lowest dissociation channel. The average recoil energy was low, only $\sim 2.5 \text{ Kcal}$, indicating that if the SF_6 molecule is highly excited before dissociation, the SF_5 fragment retains a substantial fraction of the excess energy in its internal degrees of freedom. The experimental recoil energy distribution peaks at or near zero, indicating that there is no exit barrier in the relevant dissociation channel. This observation also rules out the possibility of an "explosive" mode-controlled dissociative mechanism which would produce a velocity distribution skewed to higher energy. At higher laser energy density the SF_5 product undergoes secondary dissociation to $\text{SF}_4 + \text{F}$:

Hence the SF_6^{**} must have a lifetime shorter than the laser pulse, which was $\sim 50 \text{ ns}$. This is consistent with a theoretical (RRKM) estimate of the dissociation lifetime of SF_6^{**} with an excess energy of 20-30 kcal/mole (7-11 photons) [15]. The observed translational energy distributions are actually in quantitative agreement with the RRKM prediction with an excess energy of 20-30 kcal/mole.

Similar studies were carried out on CF_3X ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), CF Cl_3 , CF_2Cl_2 and CF_2Br_2 [14]. For the laser energy densities used in our experiments ($10\text{--}30 \text{ J/cm}^2$), the rupture of the weakest carbon-halogen bond was found to dominate in all cases. In fact, it was the only dissociation channel observed in CF_3X and CF Cl_3 (see Table 1).

As an example, laboratory angular distributions of CF_3 and Br produced in MPD of CF_3Br are shown in Fig.2. (The fragments are detected as CF_2^+ , CF^+ , and Br^+ in the mass spectrometer.) The velocity distribution of Br at a laboratory angle of 10° is shown in Fig.3. The curves have been calculated from the three theoretical translational energy distributions shown in Fig.4. The solid line, which is obtained from a standard RRKM calculation with 6 Kcal/mole excess energy, fits the data well. The other two curves are slight modi-

Table 1

Compound	Products	Endoergicity (Kcal/mole)
CF_3Cl	* $\text{CF}_3 + \text{Cl}$	86
	$\text{CF}_2 + \text{Cl} + \text{F}$	111
	$\text{CF}_2\text{Cl} + \text{F}$	124
CF_3Br	* $\text{CF}_3 + \text{Br}$	71
	$\text{CF}_2 + \text{BrF}$	95
	$\text{CF}_2\text{Br} + \text{F}$	114
CF_3I	* $\text{CF}_3 + \text{I}$	53
	$\text{CF}_2 + \text{IF}$	65
CF Cl_3	* $\text{CF Cl}_2 + \text{Cl}$	75
	$\text{CF Cl} + \text{Cl}_2$	74
CF_2Cl_2	* $\text{CF}_2\text{Cl} + \text{Cl}$	82
	$\text{CF}_2 + \text{Cl}_2$	71
CF_2Br_2	* $\text{CF}_2\text{Br} + \text{Br}$	61
	$\text{CF}_2 + \text{Br}_2$	55
N_2F_4	* 2NF_2	21
	$\text{N}_2\text{F}_3 + \text{F} (?)$	?

* observed dissociation channel

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Fig.2 Angular distributions of CF_2^+ and Br^+ mass spectrometer signals in the dissociation of CF_3Br . See Fig.4 for explanation of the curves

Fig.3 Speed distribution of Br fragment from MPD of CF_3Br at 10° from the CF_3Br beam. See Fig.4 for explanation of the curves

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Fig.4 Center-of-mass translational energy distributions for the fragments of CF_3Br

— RRKM prediction with 6 Kcal/mole excess energy
 --- modifications used in an attempt to fit the experimental data better than with the solid line
 ... to fit the experimental data better than with the solid line

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fications which illustrate the uncertainty in the theoretical fit.

The general features observed in CF_3Br are also found in the other molecules. In all cases the average translational energy released to the fragments is small, on the order of a few Kcal/mole. The translational energy distributions peak toward zero and are in good agreement with RRKM predictions assuming excitation levels with dissociation lifetimes around 1-10 ns.

CFCl_3 , like SF_6 , undergoes secondary dissociation at sufficiently high

laser energy fluence. At $\sim 5 \text{ J/cm}^2$ the products were $\text{CF Cl}_2 + \text{Cl}$ (observed as the ions CF Cl_2^+ and Cl^+), in disagreement with DEVER and GRUNWALD'S conclusion of a collisionless $\text{CF Cl}_3 \rightarrow \text{CF Cl} + \text{Cl}_2$ dissociation [4]. At higher energy fluence ($> 20 \text{ J/cm}^2$), products with high translational energy showed a smaller ratio of CF Cl_2^+ to CF Cl^+ , indicating that secondary dissociation $\text{CF Cl}_2 \rightarrow \text{CF Cl} + \text{Cl}$ had occurred. No Cl_2^+ or F^+ was detected.

N_2F_4 also undergoes simple bond rupture to form 2NF_2 . Since the N-N bond is extremely weak (21 Kcal/mole) the RRKM dissociation lifetime is $\sim 1 \text{ ns}$ for only 2 Kcal/mole excess energy. This predicts an average translational energy of the fragments of $\sim 0.4 \text{ Kcal/mole}$ which agrees well with experiment.

The similarities in lifetimes for the various molecules may be qualitatively understood as follows. The molecules will continue to absorb energy until their dissociation rate becomes comparable to the up-pumping rate due to the laser field. In our experiments with pulsewidths of $\sim 50\text{-}100 \text{ ns}$ and the dissociation yield near saturation, dissociation lifetimes on the order of 1-10 ns are expected regardless of the nature of the molecule [8b,16]. The large difference in excess energy between the halogenated methanes ($\sim 5 \text{ Kcal/mole}$) and SF_6 ($\sim 25 \text{ Kcal/mole}$) is mainly due to the larger number of vibrational degrees of freedom of the latter. It is easily seen by recalling the classical Kassel formula for the dissociation rate [17], that the rate constant is strongly dependent on the number of vibrational degrees of freedom, S.

$$K(E) = A \left(\frac{E - E_0}{E} \right)^{S-1}$$

where E and E_0 are the excitation energy and dissociation energy, respectively, and A is the Arrhenius pre-exponential factor. The exponent (S-1) is 14 for SF_6 and only 8 for the methanes, so for a given excess energy the methanes will clearly have a much greater dissociation rate than SF_6 . For molecules larger than SF_6 and similar laser pulse conditions and bond energies, much greater excess energies are expected.

It was noted above that CF_2Cl_2 and CF_2Br_2 underwent carbon-halogen bond rupture under our experimental conditions. However, Table 1 shows that the 3-center molecular elimination channel actually has lower endoergicity. It has an exit energy barrier of $\leq 10 \text{ Kcal/mole}$, but its dissociation threshold energy is still very close or even slightly lower than that of the 2-center atomic elimination channel. Then, why is the 3-center elimination not dominating in MPD of these molecules? The explanation is as follows. The 3-center elimination is expected to proceed through a much "tighter" critical configuration than the 2-center carbon-halogen bond dissociation (i.e., the 3-center critical configuration should be characterized by higher vibrational frequencies and lower density of states than the 2-center case). Consequently the rate of 2-center elimination should grow much faster with excess energy than the rate of 3-center elimination. At an excitation level of 5-10 Kcal above the dissociation threshold, which was provided by our laser energy fluence of $\sim 10 \text{ J/cm}^2$ the 2-center elimination already dominates. This is what we observe experimentally. Using a lower energy fluence ($1.5\text{-}6 \text{ J/cm}^2$) which produces a lower excitation level above threshold, KING and STEPHENSON [17] observe around 15% of the dissociation of CF_2Cl_2 through the 3-center elimination channel. Therefore within the framework of statistical unimolecular reaction rate theory the laser chemist may still have some control over the branching ratio between nearby competing dissociation channels. This effect is actually common in pyrolysis studies where additional dissociation channels may open up at higher temperatures, although with lasers more precise

control of the reaction should be possible.

Preliminary results on C_2F_5Cl [14a] show roughly a 2:1 branching ratio for rupture of the C - Cl bond (83 Kcal) compared to the C - C bond (97 Kcal). RRKM calculations predict a branching ratio of $\sim 1.5:1$ for an energy excess of 50 Kcal above the C - Cl bond dissociation energy (corresponding to lifetimes around 10-15 ns) and $\sim 1:1$ for a 60 Kcal energy excess (lifetimes ~ 1 -2 ns). A detailed study of this system at various laser intensities and energy fluences is planned.

B. HCl Elimination Reactions

We have observed 3-center and 4-center elimination of HCl in MPD of CHF_2Cl , $CHFCF_2$, $CHClCF_2$, CH_3CCl_3 and CH_3CF_2Cl [14]. This is the dissociation channel which is of the lowest activation energy in each case. With the exception of $CHClCF_2$, the observed translational energy distribution peaks at a finite energy due to the existence of appreciable back reaction (or exit-barriers) for these systems. Without additional assumptions, the RRKM theory may not be expected to yield the correct translational energy distributions of the dissociation products, since the disposal of the back reaction potential barrier energy into vibrational, rotational, and translational energy of the products depends on the detailed structure of the potential surface in the vicinity of the critical configuration. However, the RRKM theory should still give a reasonable estimate of the excess energy in the molecule for a given dissociation lifetime if the excitation energy is completely randomized.

A level diagram for CH_3CCl_3 which undergoes 4-center elimination is shown in Fig.5. CH_2CCl_2 was detected in the mass spectrometer as $CH_2CCl_2^+$ and HCl

Fig.5 Energy level diagram for the dissociation of CH_3CCl_3

as HCl^+ . No CH_3^+ , $CH_3CCl_2^+$, CH_3CCl^+ or $CH_2CCl_2^+$ was observed. Since the CH_2CCl_2 fragment is highly vibrationally excited, the electron bombardment in the mass spectrometer readily decomposes it, yielding much less $CH_2CCl_2^+$ than is normally observed at room temperature [19]. The fact that the velocity distributions of HCl and CH_2CCl_2 were correctly related by momentum conservation provides a definitive check that CH_2CCl_2 and HCl were the dissociation products. We also have evidence for some secondary dissociation of $CH_2CCl_2 \rightarrow CHCCl + HCl$ at higher laser energies.

Figure 6 shows the experimental speed distribution of CH_2CCl_2 (detected as $CH_2CCl_2^+$) at various angles, as well as the speed distribution of the primary CH_3CCl_3 beam. The angular distribution of CH_2CCl_2 is shown in Fig.7. The translational energy distributions of the fragments in Fig.8 were generated from the expression $P(E) = (E - a)^2 \exp(-3(E - a)/b)$ to fit the experimental

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Fig.6 Speed distributions of CH_2CCl_2 at various angles. (The curves are normalized to give the same angular distribution at 10°)

o Experiment

— $a = 0$ Kcal/mole, $b = 9$ Kcal/mole

... $a = 0$ Kcal/mole, $b = 9$ Kcal/mole

--- $a = 1$ Kcal/mole, $b = 7$ Kcal/mole

$$P(E) = (E - a)^2 \exp \frac{-3(E - a)}{b}$$

XBL 7711-10898 A

Fig. 7 Angular distribution of CH₂CCl₂ (symbols same as in Fig. 6) the curves are normalized to the same value at 10°

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Fig. 8 Translational energy distributions for the fragments from CH₃CCl₃ in the center-of-mass frame of the parent (symbols same as in Fig. 6, plus ---: RRKM distribution). The curves are normalized to their peak values

speed and angular distributions, where a and b are adjustable parameters. For comparison, the translational energy distribution obtained from an RRKM calculation with a dissociation lifetime of 10 ns is also presented (arbitrarily shifted from zero energy by 5 Kcal/mole). This RRKM translational energy distribution is clearly much too narrow since the calculation neglects the interaction between the fragments beyond the critical configuration. However, the average excess energy deduced from the calculation is still reliable and corresponds to 22 Kcal/mole above the dissociation threshold. Adding to it the back reaction barrier energy of 42 Kcal/mole, the total excess energy is around 64 Kcal/mole. The average translational energy of the fragments from Fig. 8 is only 8 Kcal/mole, corresponding to 10-15% of the total excess energy

(or 20% of the exit channel potential barrier). Very similar results were obtained with $\text{CH}_3\text{CF}_2\text{Cl}$. Evidently a large fraction (> 85%) of the total excess energy in 4-center eliminations must be left as internal excitation of the fragments. Much of this internal energy should appear as vibrational energy in CH_2CCl_2 and HCl . In fact, BERRY and PIMENTEL [20] have observed laser emission from vibrationally excited HF produced in a similar 4-center elimination reaction of CH_3CF_3 .

Our best results on 3-center elimination were obtained with CHF_2Cl . There is a 6 Kcal/mole barrier to back reaction in this case and the RRKM calculation predicts a 7 Kcal/mole excess energy above the barrier for a dissociation lifetime of 10 nsec. Of the total excess energy of 13 Kcal/mole, we found an average of 8 Kcal/mole in translational energy. Using laser induced fluorescence, KING and STEPHENSON [18] have deduced the internal energy distribution of the CF_2 fragment from MPD of CHF_2Cl . They found that the internal energy distribution in CF_2 was characterized by a vibrational temperature of 1160 K and a rotational temperature of around 2000 K. From the time-dependent reduction of CF_2 concentration in the radiation zone due to diffusion of CF_2 they deduced an average translational energy of CF_2 of 6.9 Kcal/mole by assuming a Maxwellian velocity distribution for CF_2 or 3.5 Kcal/mole by assuming a δ -function velocity distribution. The latter value agrees with what we found for CF_2 , namely 3.5 Kcal/mole out of the total average translational energy of 8 Kcal/mole of both fragments CF_2 and HCl . Their results on the internal energy distribution together with our results on the translational energy distribution provide the most detailed description of energy partitioning in a unimolecular reaction to date. The high rotational energy of CF_2 suggests that a non-central, repulsive force between CF_2 and HCl exists on the product side of the exit barrier.

Concluding Remarks

In addition to its possible practical applications to isotope separation, infrared multiphoton excitation has become a clean and elegant method of preparing highly energized molecules for studies of unimolecular reaction dynamics. However, results in the literature are often confused by collisional effects. The difficulty can be eliminated in the molecular beam environment. Our crossed laser and molecular beams studies have not provided any evidence for "mode-selective" chemistry. The reaction generally proceeds through the lowest dissociation channel; although it appears that some control over the branching ratio into nearby dissociation channels is possible by varying the excitation conditions. This control is still within the framework of the statistical reaction theory.

For the simple bond dissociation reactions, the RRKM theory satisfactorily predicts both the excess energy above the dissociation threshold and the translational energy distribution of the products. The excess energy depends critically on the strength of the bond being broken and on the number of vibrational degrees of freedom in the molecule. Most of the excess energy goes into internal degrees of freedom of the products because of their strong contribution to the density of states.

In the elimination reactions the translational energy distribution alone is not sufficient to characterize the dynamics of the reaction. Complementary information on the internal energy distributions in the products, such as those obtained by KING and STEPHENSON on CF_2 using laser induced fluorescence, is needed. Other techniques, such as infrared chemiluminescence, double resonance and excited-state photoionization spectroscopy, may also be

used in conjunction with molecular beam experiments to further our understanding of unimolecular reaction dynamics.

The availability of high pulse rate CO₂ lasers should permit beam experiments which were previously not feasible due to a low excitation duty cycle. As one example, it should be possible to see a clear difference between photoionization curves of thermally excited and laser excited polyatomic molecules if the infrared multiphoton excitation process produces a non-thermal vibrational energy distribution, as recently predicted on the basis of our model calculations [8b].

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