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CROSSED LASER AND MOLECULAR BEAM STUDY OF
MULTIPHOTON DISSOCIATION OF C$_2$F$_5$Cl

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Recent molecular beam experiments [1] have shown that infrared multiphoton dissociation of molecules mainly proceeds through the lowest available dissociation channel. Larger molecules may have the two (or more) lowest dissociation channels close in energy. When the laser energy fluence is adequate, the molecules can be excited above the dissociation energies of all these channels, with the branching rate into each available dissociation channel determined by statistical considerations since the excitation energy is expected to be randomized rapidly. In the case of C$_2$F$_5$Cl two competing dissociation channels exist: Cl atom elimination at 83 kcal/mole and C-C bond rupture at 97 kcal/mole. Although C-C bond rupture has appreciably higher dissociation energy, with three more rotational degrees of freedom in the fragments, the rate constant is expected to increase faster than Cl elimination when the excitation energy becomes higher. Consequently, the ratio of Cl elimination to C-C rupture will be a good indicator of the level of excitation. RRKM rate constants for dissociation into these channels are shown in Fig.1.

![Graph showing rate constants for dissociation of C$_2$F$_5$Cl as a function of total energy in the molecule.](image-url)
We have investigated the multiphoton dissociation of C_2F_5Cl using a crossed laser molecular beam apparatus with a rotatable mass spectrometer detector [2]. The yield in each dissociation channel as a function of laser energy fluence is shown in Fig.2. C_2F_5 produced in the Cl atom elimination is detected as C_2F_4^+, and CF_2Cl from the C-C bond rupture is detected as CF_2Cl^+. At low laser energy fluence the Cl atom elimination dominates. As the energy fluence is increased this channel rapidly saturates, while the dissociation into CF_3 + CF_2Cl becomes more prominent. Fig.3 shows data taken with the laser beam focused more tightly on the molecular beam to achieve higher energy fluence. The persistence of the C_2F_4^+ signal at

![Graph](image1)

**Fig.2** Yield of C_2F_4^+ (from C_2F_5) and CF_2Cl^+ (from CF_2Cl) vs. laser energy fluence at θ = 15° in the laboratory.

![Graph](image2)

**Fig.3** Yield of C_2F_4^+ (from C_2F_5) and CF_2Cl^+ (from CF_2Cl) vs. laser energy fluence at θ = 15° in the laboratory.
an energy fluence of $\sim 30 \text{ J/cm}^2$ indicates that secondary dissociation of $\text{C}_2\text{F}_5$ into $\text{C}_2\text{F}_4 + \text{F}$ or $\text{CF}_3 + \text{CF}_2$ is minor ($\text{C}_2\text{F}_4$ mainly ionizes into $\text{C}_2\text{F}_3^+$).

The dynamics of the two dissociation channels has been studied by measuring the angular and velocity distributions of the products. Theoretical product translational energy distributions may then be tried to reproduce the experimental data. For the Cl atom elimination the center-of-mass translational energy distribution peaks at zero energy and can be described by a statistical model. The C-C bond scission appears to have a small barrier in the exit channel, indicated by a peaking of the translational energy distribution at a non-zero energy. The consistency of the level of excitation derived from fragment translational energy distributions and that implied from the ratio of two decomposition channels using RRKM theory is now under investigation.

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References

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