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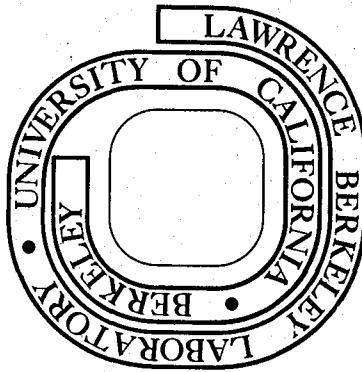
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MULTIPHOTON DISSOCIATION PRODUCTS FROM
HALOGENATED HYDROCARBONSAa. S. Sudbo,[†] P. A. Schulz,[†] E. R. Grant,^{*,‡}
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The recent interest in multiphoton dissociation (MPD) of polyatomic molecules has revealed quite a bit of confusion as to what the major dissociation channels of some molecules are,¹⁻⁵ and whether the dissociation process can be described by a statistical, e.g., RRKM, theory of unimolecular reactions.⁴⁻⁸ In a gas cell experiment an experimenter often finds great difficulties in answering questions such as: do vibrationally excited molecules react with one another, how do reactions involving free radicals produced in the dissociation proceed, can these radicals decompose further in the presence of the laser field, and does the detection method used actually probe the primary dissociation channel.

Using the molecular beam setup previously described,⁹ we have overcome most of these difficulties. We have studied MPD of a number of compounds, mainly halogenated methanes, ethanes and ethylenes, and identified their major dissociation channels. To identify an MPD

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product, we realize that a unique set of ratios between mass spectrometer signals of various ion fragments must first be established for a given molecular species or radical, and preferably the velocity distributions of the dissociation products should be measured and checked for consistency. In our setup, we could measure both angular and time-of-flight distributions for the fragments, and perform this check. The low density of molecules in the beam and the extremely low duty cycle in our experiment prevented us from observing the competing minor channels which have very small branching ratios (< 0.1).

In Table 1 we give a list of the molecules we have studied, together with the results and a few parameters describing the experimental conditions. The purpose of heating the nozzle in some of the experiments was to increase the hot-band absorption and thus shift the absorption frequency to a value more easily attainable by our CO₂ TEA laser. A more extensive presentation and analysis of our data will be given elsewhere; here we present only the qualitative results.

The simplest compounds studied were the members of the CF₃X series, X = Cl, Br, I. The fragments of MPD were CF₃⁺, detected in the mass spectrometer mainly as CF₂⁺ and CF⁺, both with identical velocity distributions, and X with a different distribution. The velocity distributions of CF₃ (detected as CF₂⁺ and CF⁺) and X were correlated by the conservation of linear momentum in the dissociation

process. The ratios between the mass spectrometer signals of CF_3^+ , CF_2^+ and CF^+ were determined for each of the three cases. The ratios were independent of laser energy fluence and the product translational energy (within the stated uncertainties). With an ionizing electron energy of 200 eV in the mass spectrometer, the ratios were

X	CF_3^+	CF_2^+	CF^+
Cl	0.2 ± 0.2	2.4 ± 0.2	1.0
Br	0.2 ± 0.3	2.4 ± 0.1	1.0
I	0.7 ± 0.2	2.6 ± 0.2	1.0

The species CF_2Cl_2 , CF_2Br_2 , C_2HCl_3 also mainly dissociate through the rupture of a carbon halogen bond. Molecular elimination forming $\text{CF}_2 + \text{Cl}_2$ and $\text{CF}_2 + \text{Br}_2$ from CF_2Cl_2 and CF_2Br_2 were found not to be the major dissociation channels.^{1,2} For CFCl_3 , however, as previously reported for SF_6 ,⁸ we observed an ionization pattern that depended on laser energy fluence and the product translational energy. At moderate ($\approx 5 \text{ J/cm}^2$) laser energy fluence the products could be identified as CFCl_2 and Cl , through the observation of the ions CFCl_2^+ and Cl^+ . Our result agreed with Hudgens' observation,¹ but not with Dever and Grunwald's conclusion of $\text{CFCl}_3 \rightarrow \text{CFCl} + \text{Cl}_2$.⁴ However, at higher energy fluence ($> 20 \text{ J/cm}^2$), products with very high translational energy showed appreciably less relative fraction of CFCl_2^+ as compared to CFCl^+ , indicating that CFCl_2 dissociated further to form CFCl and Cl . No F^+ or Cl_2^+ could be detected throughout this experiment.

Similar analysis has been performed for the other molecules listed in Table 1. Here we will just briefly comment on the general

features we have observed. A number of our systems showed hydrogen halide (i.e., HCl) elimination (in some cases expected on the basis of observed pyrolytic unimolecular reactions). The translational energy distribution of HCl in all cases, with the exception of CHCl:CF_2 , indicated an exit potential energy barrier of the order of a few kcal/mole.

Especially interesting cases are some of the compounds containing two carbon atoms, because we observed competing dissociation channels. They were inferred on the basis of observation of fragments in the mass spectrometer which could not have all been present if there were only one channel, and also from their unique velocity distribution. Table 1 lists some of the observed fragment ions for these molecules. None of our observations seemed to contradict the assumption that dissociation always proceeds through the channel(s) with the lowest dissociation threshold, i.e., the endoergicity plus exit potential energy barrier.

In conclusion we have found that our experimental results, including the velocity distributions of fragments which will be reported elsewhere, strongly support the idea that multiphoton dissociation of molecules produces fragments mainly through the lowest-energy dissociation channel, as one would expect for molecules with randomly distributed excitation energy. Our data is not as yet fully analyzed, but so far, we have not seen any evidence that the process is qualitatively different from what can be adequately described by a statistical theory of unimolecular reactions.

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Table 1

Molecule, Fragments and Observed Ions	Absorption Frequency (cm ⁻¹)	Exciting Frequency (cm ⁻¹)	Beam Nozzle Temperature °C
$\text{CF}_3\text{Cl} \rightarrow \text{CF}_3 + \text{Cl} (\text{Cl}^+, \text{CF}_2^+)$	1106	1090.0	240 °C
$\text{CF}_3\text{Br} \rightarrow \text{CF}_3 + \text{Br} (\text{Br}^+, \text{CF}_2^+)$	1082	1078.6	25 °C
$\text{CF}_3\text{I} \rightarrow \text{CF}_3 + \text{I} (\text{I}^+, \text{CF}_2^+)$	1076	1073.3	25 °C
$\text{CF}_2\text{Cl}_2 \rightarrow \text{CF}_2\text{Cl} + \text{Cl} (\text{Cl}^+, \text{CF}_2\text{Cl}^+)$	1098, 923	1089.0, 925.1	25 °C, 310 °C
$\text{CF}_2\text{Br}_2 \rightarrow \text{CF}_2\text{Br} + \text{Br} (\text{Br}^+, \text{CF}_2\text{Br}^+)$	1090	1084.6	25 °C
$\text{CHF}_2\text{Cl} \rightarrow \text{CF}_2 + \text{HCl} (\text{HCl}^+, \text{CF}_2^+)$	1116, 1160	1082.3	280 °C
$\text{CHFCl}_2 \rightarrow \text{CFCl} + \text{HCl} (\text{HCl}^+, \text{CFCl}^+)$	1070	1055.6	290 °C
$\text{CFCl}_3 \rightarrow \text{CFCl}_2 + \text{Cl} (\text{Cl}^+, \text{CFCl}_2^+)$ └── $\text{CFCl} + \text{Cl} (\text{CFCl}^+)$	1090	1074.6	25 °C
$\text{CHClCF}_2 \rightarrow \text{C}_2\text{F}_2 + \text{HCl} (\text{HCl}^+)$ └── $\text{CHCF}_2 + \text{Cl} (\text{CHCF}_2^+)$	970	967.7	25 °C
$\text{C}_2\text{HCl}_3 \rightarrow \text{C}_2\text{HCl}_2 + \text{Cl} (\text{C}_2\text{HCl}_2^+)$	930	929.1	80 °C
$\text{CF}_3\text{CF}_2\text{Cl} \rightarrow \text{CF}_3\text{CF}_2 + \text{Cl} (\text{Cl}^+, \text{C}_2\text{F}_4^+)$ └── $\text{CF}_3 + \text{CF}_2\text{Cl} (\text{CF}_2\text{Cl}^+)$	982	978.5	25 °C
$\text{CH}_3\text{CF}_2\text{Cl} \rightarrow \text{CH}_2\text{CF}_2 + \text{HCl} (\text{HCl}^+, \text{CF}^+)$	963	956.2	280 °C

Table 1 (Continued)

<u>Molecule, Fragments and Observed Ions</u>	<u>Absorption Frequency (cm⁻¹)</u>	<u>Exciting Frequency (cm⁻¹)</u>	<u>Beam Nozzle Temperature °C</u>
$\text{CH}_3\text{CCl}_3 \rightarrow \text{CH}_2\text{CCl}_2 + \text{HCl} (\text{HCl}^+, \text{CH}_2\text{CCl}_2^+)$	1075	1073.3	25°C
$\text{SF}_6 \rightarrow \text{SF}_5 + \text{F} (\text{SF}_3^+, \text{SF}_2^+)$ $\rightarrow \text{SF}_4 + \text{F} (\text{SF}_3^+, \text{SF}_2^+)$	948	944.2	25°C
$\text{N}_2\text{F}_4 \rightarrow 2\text{NF}_2 (\text{NF}_2^+, \text{NF}^+)$	998	975.9	25°C

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