# Infrared Multiphoton Absorption and Reaction of 2-Chloro-1,1,1-trifluoroethane

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The infrared multiphoton absorption and dissociation of CF<sub>3</sub>CH<sub>2</sub>Cl has been studied by measuring the dependence of the reaction probability and product distribution on the laser fluence and bath gas pressure. Absorption measurements were performed at two laser frequencies to establish the absorbed laser energy; the absorption measurements displayed Beer's law behavior except at very low laser fluence. Sensitized reactions with SiF4 were conducted for comparison to the direct laser-induced process; the effective temperature within the irradiated volume for the  $SiF_4$  experiments was determined as a function of incident laser energy. The three main reaction channels are four-centered HF elimination, three-centered HCl elimination, and C-Cl homolysis; the product ratios were very dependent on the incident laser fluence. Addition of toluene as a bath gas significantly lowered the reaction probability, especially at lower laser fluence, but had only a minor influence on the product distribution. The infrared laser-induced energy absorption and reaction processes of CF<sub>3</sub>CH<sub>3</sub>, CF<sub>3</sub>CH<sub>2</sub>Cl, and CF<sub>3</sub>CH<sub>2</sub>Br are compared. The data provide evidence for a fluence-dependent fractionation of absorbed laser energy producing a two-component energy distribution for the former two compounds.

## Introduction

Excitation of polyatomic molecules in the gas phase with intense, pulsed, infrared laser radiation can lead to multiphoton absorption and subsequent reaction.<sup>1-7</sup> Interest has been directed toward the basic nature of the multiphoton absorption process, energy distributions resulting from laser absorption, laser-induced elementary reactions, and applications to isotope separation and sample purification. The mechanism of infrared multiphoton absorption has received considerable attention but many questions remain.

In previous work, we have investigated molecules that can be broadly classified as "small" and "large" based on the qualitative nature of their absorption of energy from the laser field.<sup>1-4</sup> The absorption of laser energy by the small molecules CH<sub>3</sub>CF<sub>3</sub> and CH<sub>3</sub>CH<sub>2</sub>F did not follow Beer's law; rather the absorption cross section increased with both parent and inert gas pressure.<sup>8,9</sup> The increase of the bulk laser absorption cross section,  $\sigma_{\rm L}(\phi)$ , with pressure can be explained most readily as collisional rotational relaxation during the laser pulse. A second feature is that the low-pressure limiting laser cross sections,  $\sigma_L^{0}(\phi)$ , were a factor of 2-3 smaller than the conventional broad-band cross sections even at very low laser fluence. The  $\sigma_1^{0}(\phi)$  values decreased very sharply with increase of  $\phi$  at low fluence and became constant at high  $\phi$ . A third characteristic of small molecules is a reduction in  $\sigma_{\rm L}(\phi)$  for short laser pulses, i.e., a dependence of  $\sigma_{\rm L}(\phi)$  on laser intensity, which could be consistent with either anharmonicity or

5431 (1982).

saturation. Since the shorter laser pulse (at constant  $\phi$ ) has higher intensity and larger power broadening, a larger  $\sigma_{I}(\phi)$  in fact would be expected because the fraction of the rotational population absorbing the laser energy should be larger, if there was no anharmonicity and no saturation.

In contrast, the "large" organic esters, 1-4 CF<sub>3</sub>CH<sub>2</sub>Br, 9 CH<sub>3</sub>C-HBrCH<sub>3</sub>,<sup>9</sup> CH<sub>3</sub>CHClCH<sub>3</sub>,<sup>9</sup> and CH<sub>3</sub>CHClCH<sub>2</sub>CH<sub>3</sub><sup>9</sup>, exhibited Beer's law behavior and neither collisionally enhanced absorption nor extensive red-shifting of the laser absorption band was observed. Other laboratories also have reported similar findings for large molecules.<sup>10,11</sup> The greater simplicity of the large molecule behaviour appears to results from the much smaller discrete region or, conversely, the onset of the quasicontinuum at lower internal energy. Since the multiphoton absorption by large molecules appears simpler at the experimental level than for small molecules, it is possible to deduce microscopic cross sections from the  $\sigma_{\rm L}(\phi)$ and reaction probability,  $P(\phi)$ , data. A direct consequence of the characteristic laser energy absorption by large molecules is that  $P(\phi)$  increases rapidly with  $\phi$  and frequently approaches unity. However, for ethyl acetate and ethyl fluoroacetate, the  $P(\phi)$  for the same amount of absorbed energy depended on laser frequency and  $\phi^2$ . This was evidence that only a certain, fluence-dependent, fraction of molecules absorb the laser energy.

We have suggested in the earlier studies<sup>9</sup> that the density of rotational states is an important molecular property for distinguishing between "small" and "large" molecules. A high density of rotational states and the availability of several low-frequency modes to aid the anharmonic coupling appear to be the critical factors leading to the apparent homogeneous behavior of the absorption bands for large molecules. The sparse density of rotational states combined with power broadening and dynamic Stark shifting by the laser field must be responsible for the small molecule constraints.

In the present work, we studied CF<sub>3</sub>CH<sub>2</sub>Cl, which is in the transition regime between small, e.g., CF<sub>3</sub>CH<sub>3</sub>, and large, e.g.,  $CF_3CH_2Br$ , molecule behavior. Both energy absorption and  $P(\phi)$ measurements are reported from  $\phi = 0.2-5.5 \text{ J/cm}^2$ . This compound possesses three reaction channels (eq 1-3) and provides an interesting case for the study of parallel competing unimolecular

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<sup>(11)</sup> C. N. Plum and P. L. Houston, Chem. Phys., 45, 159 (1980).

$$CF_{3}CH_{2}CI \xrightarrow{\alpha, a-elimination} HF + CF_{2} = CHCI \qquad (1)$$

$$CF_{3}CH_{2}CI \xrightarrow{\alpha, a-elimination} HCI + CF_{3}CH \rightarrow CF_{2} = CHF \qquad (2)$$

$$C-CI homolysis CI + CF_{3}CH_{2} \xrightarrow{-F} CF_{2} = CH_{2} \qquad (3)$$

reactions with different magnitudes of preexponential factors. Sensitized reactions with  $SiF_4$  were done in order to help characterize the three reaction channels.

The thermal unimolecular reaction of CF<sub>3</sub>CH<sub>2</sub>Cl has been studied by the shock tube method by Millward and Tschuikow-Roux<sup>12</sup> and by the chemical activation method by Holmes.<sup>13</sup> In the chemical activation work, CF<sub>3</sub>I and ICH<sub>2</sub>Cl were photolyzed and the recombination of CF<sub>3</sub> and CH<sub>2</sub>Cl formed chemically activated CF<sub>3</sub>CH<sub>2</sub>Cl\* with  $\langle E \rangle = 100$  kcal/mol; the total deactivation rate constant was ~5.3 × 10<sup>6</sup> s<sup>-1</sup> with  $k_1:k_2:k_3$  of 1.0:0.6:0.3.

## **Experimental Section**

A Lumonics Model 103 TEA CO<sub>2</sub> laser was used with an aperture to give a nearly constant energy density beam. The energy of the laser pulse was measured by a precalibrated Scientech energy meter, Model 38-0102. A fluence of 0.5–1.3 J/cm<sup>2</sup> at 1084.6 cm<sup>-1</sup> [R(30) line of 001–020 band] could be obtained without focusing. The fluence was reduced by placing successive layers of plastic film between the sample and laser. For  $\phi$  of 1.0 to 3.8 J/cm<sup>2</sup>, a Galilean telescope consisting of two BaF<sub>2</sub> lenses was utilized. For  $\phi$  higher than 3.8 J/cm<sup>2</sup>, a single long focal length (f = 75 cm) lens was used, i.e., no second lens was inserted to make the laser beam parallel. The  $\sigma_L(\phi)$  were measured with a dual pyroelectric detector arrangement as described in detail in our earlier work.<sup>2</sup> Since Beer's law was followed, the absorption was measured from 0.5 to 30 torr.

All experiments were performed with gas-phase samples of  $CF_3CH_2Cl$  (PCR Research Chemicals, Inc.) which contained <1% of  $CF_2Cl_2$ . Samples of  $CF_2$ —CHF,  $CF_2$ —CHCl,  $CF_2$ —CH2,  $SiF_4$  (PCR Research Chemicals, Inc.), and toluene (Fisher Scientific Co.) were degassed and distilled under vacuum prior to storage in Pyrex containers. The samples were irradiated in vessels of 3.8 cm diameter and 3.0 cm length; thus, the fluence was uniform. The diameter of the irradiated part of the cell was measured with burn paper; the uncertainty in the diameter of the irradiated volume is significant, approximately  $\pm 0.5$  mm. For experiments with  $CF_3CH_2Cl$  alone, the pressure was always 0.05 torr.

The reactant and products from the multiphoton laser-induced unimolecular reaction were monitored with a Varian Model 2700 gas chromatograph equipped with a flame ionization detector. A 5 ft  $\times$  <sup>1</sup>/<sub>8</sub> in. diameter column packed with Porapak Q and operated with a 55 mL/min flow rate of helium carrier gas at 70–80 °C was used to separate the components. The products from laser irradiation were identified (with real samples) by GC-mass spectroscopy employing a Finnigan Model 4000 instrument.

# Results

1. Direct Laser-Induced Reaction of  $CF_3CH_2Cl$ . Most experiments were performed by irradiating 0.05 torr of  $CF_3CH_2Cl$  at 1084.6 cm<sup>-1</sup>, which is on the low-frequency side of the  $CH_2$  twisting absorption band. For pressure <0.05 torr, the thermal contribution, defined as in our earlier studies,<sup>2,3</sup> to the yield should be negligible. The three main products  $CF_2$ — $CH_2$ ,  $CF_2$ —CHF, and  $CF_2$ —CHCl were identified by comparing gas chromatographic retention times with the pure substances and by GC-mass spectroscopy. For  $\phi > 1.5$  J/cm<sup>2</sup> additional minor products were observed, and they constitute 2–5% of the total yield. Although identification was not positive, the minor products seemed to be consistent with  $CF_2$ — $CF_2$ ,  $CF_3$ ,  $CF_2$ —CFCl, and  $CF_3CH$ — $CF_2$  based upon GC-MS data.

A. Dependence of Reaction Probability and Product Distribution on  $\phi$ . The  $P(\phi)$  for CF<sub>3</sub>CH<sub>2</sub>Cl per laser pulse exhibited



Figure 1. The reaction probability,  $P(\phi)$ , vs. laser fluence for reaction of CF<sub>3</sub>CH<sub>2</sub>Cl, CF<sub>3</sub>CH<sub>2</sub>Br, and CF<sub>3</sub>CH<sub>3</sub> at 0.05 torr.



Figure 2. Fractional percentage of three main products vs. laser fluence for reaction of 0.05 torr of  $CF_3CH_2Cl$  irradiated at 1084.6 cm<sup>-1</sup>.

a strong dependence on  $\phi$ , as is common for such multiphoton processes.<sup>1,2</sup> The  $P(\phi)$  was observed to vary as  $\phi^n$  with  $n \sim 3$ ;  $P(\phi) \sim 0.80$  occurred at  $\phi = 5.3$  J/cm<sup>2</sup>. There was no significant difference in data collected from experiments utilizing either the Galilean telescope or single-lens focusing configuration. A plot of  $P(\phi)$  vs.  $\phi$  for CF<sub>3</sub>CH<sub>2</sub>Cl is given in Figure 1; data for CF<sub>3</sub>CH<sub>3</sub> and CF<sub>3</sub>CH<sub>2</sub>Br are also plotted for discussion purposes (vide infra).

The product distribution from irradiation of  $CF_3CH_2Cl vs. \phi$ is shown in Figure 2. All products increased with fluence but the relative fractions of  $CF_2$ — $CH_2$  and  $CF_2$ —CHF also increased with increasing fluence. It was observed that  $CF_2$ — $CH_2$  increased at the expense of  $CF_2$ —CHCl with a crossover in yields at ~3.8 J/cm<sup>2</sup>. The yields of  $CF_2$ — $CH_2$  and  $CF_2$ —CHF approached zero at low laser fluences indicating that  $CF_2$ —CHCl arose from the

<sup>(12)</sup> G. C. Millward and E. Tschuikow-Roux, Int. J. Chem. Kinet., 4, 559 (1972).

<sup>(13)</sup> B. E. Holmes, private communication.



**Figure 3.** Reaction probability (left scale) and product distribution (right scale) vs. added toluene for CF<sub>3</sub>CH<sub>2</sub>Cl irradiated at 1084.6 cm<sup>-1</sup> and 3.4 J/cm<sup>2</sup>.  $P_0(\phi)$  is the reaction probability in the absence of toluene;  $P(\phi)$  is the reaction probability at the indicated pressure of toluene.

# lowest threshold energy channel.

B. Dependence of Reaction Probability and Product Distribution on Added Toluene. Toluene was used as both a free radical scavenger and a quenching gas in the laser-induced reaction of CF<sub>3</sub>CH<sub>2</sub>Cl. It was considered conceivable that, especially at high  $\phi$ , a contribution to  $P(\phi)$  might result from consumption of CF<sub>3</sub>CH<sub>2</sub>Cl by free radical chain processes. To check for this, experiments were performed with 0.025 torr of toluene added to 0.05 torr of CF<sub>3</sub>CH<sub>2</sub>Cl. This pressure of toluene should cause no significant quenching but should eliminate radical processes. The  $P(\phi)$  results were unaffected by the toluene assuring that  $P(\phi)$  reflects only direct laser-induced reaction.

The effect of higher pressures of toluene on product yields and ratios is illustrated in Figure 3. The  $P(\phi)$  data are presented as a Stern-Volmer type plot, i.e., a graph of the ratio of the reaction probability in the absence of the added gas,  $P_0(\phi)$ , to that in the presence of toluene,  $P(\phi)$ , vs. pressure of added toluene. Experiments were conducted<sup>14</sup> at  $\phi = 1.6$  and 3.4 J/cm<sup>2</sup>, although only data from the higher fluence are presented in Figure 3. At the higher fluence, a higher pressure of toluene is required to produce an equivalent amount of quenching; e.g., at  $\phi = 1.6$  J/cm, only 0.5 torr of toluene is needed to produce  $P_0(\phi)/P(\phi) = 10$ but 9 torr is necessary at  $\phi = 3.4$  J/cm.<sup>2</sup>

The fractional distributions of the three main products were not affected by adding toluene, as evidenced by Figure 3, even though the absolute reaction yields were reduced by large factors. These data conclusively demonstrate the absence of bimolecular free-radical pathways for product formation in the laser-induced reaction of  $CF_3CH_2Cl$ .

II. SiF<sub>4</sub>-Sensitized Reactions of CF<sub>3</sub>CH<sub>2</sub>Cl. A. Dependence of Reaction Probability and Product Distribution on  $\phi$ . Sensitized reactions were performed with mixtures of 0.4 torr of CF<sub>3</sub>CH<sub>2</sub>Cl and 5.0 torr of SiF<sub>4</sub> to confirm the three major unimolecular reaction pathways. The laser energy was deposited into the SiF<sub>4</sub> sensitizer by irradiation at 1027.4 cm<sup>-1</sup> [P(40) of 001–020 band]. The 0.74-cm-diameter laser beam was unfocused and plastic film reduced  $\phi$  to 0.2–0.6 J/cm<sup>2</sup>. The  $P(\phi)$  increased from 0.002 to 0.4 for  $\phi = 0.2$  to 0.6 J/cm<sup>2</sup>. From the viewpoint of the reaction probability at the same fluence, the sensitization reaction gave approximately 100 times higher reaction probability than for the direct laser-induced reaction because of the larger absorption cross section of SiF<sub>4</sub> and the thermal nature of the reaction, which give a longer reaction period before cooling.



Figure 4. Fractional percentage of three main products vs. laser fluence for reaction of 0.4 torr of  $CF_3CH_2Cl$  sensitized with 5.0 torr of  $SiF_4$  by irradiation at 1027.4 cm<sup>-1</sup>. Solid lines indicate experiments without toluene; dashed lines show experiments with 0.14 torr added toluene.



Figure 5. Ratios of  $CF_2$ —CHCl/CF<sub>2</sub>—CHF and  $CF_2$ —CHCl/CF<sub>2</sub>— CH<sub>2</sub> vs. laser fluence. The temperature designations are calculated as described in Appendix II.

There was no reaction for SiF<sub>4</sub>-sensitized mixtures of CF<sub>2</sub>= CHF, CF<sub>2</sub>=CHCl, or CF<sub>2</sub>=CH<sub>2</sub> in separate experiments. Secondary reactions from these products of the CF<sub>3</sub>CH<sub>2</sub>Cl reaction, therefore, need not be considered.

The fractional percentages of the three main products vs.  $\phi$  for the SiF<sub>4</sub>-sensitized reaction are depicted in Figure 4. As with the direct laser-induced reaction, the relative yield of CF<sub>2</sub>=CHCl declines and that of CF<sub>2</sub>=CHF and CF<sub>2</sub>=CH<sub>2</sub> increases with increasing  $\phi$ . However, in the sensitized reaction the CF<sub>2</sub>=CHF yield exceeds the CF<sub>2</sub>=CH<sub>2</sub> yield and the converse is true for the direct laser-induced reaction. This is similar to the shock tube results and suggests the possibility of some free-radical-induced reactions. Therefore, some sensitized experiments were done with toluene as a free-radical inhibitor.

B. Sensitized Reactions of  $CF_3CH_2Cl$  with Added Toluene. Sensitized experiments with  $CF_3CH_2Cl:SiF_4$ :toluene mixtures of 0.4:5.0:0.14 composition were conducted for  $\phi = 0.2-0.6$  J/cm<sup>2</sup>. The  $P(\phi)$  was independent of the added toluene, as would be expected for a thermal unimolecular reaction. Figure 4 depicts the fractional percentage of the main reaction products for the



**Figure 6.** Bulk laser absorption cross sections,  $\sigma_L(\phi)$ , vs. laser fluence for CF<sub>3</sub>CH<sub>2</sub>Cl at 1084.6 (O) and 1092.0 cm<sup>-1</sup> ( $\oplus$ ), CF<sub>3</sub>CH<sub>3</sub> at 1076.0 ( $\blacktriangle$ ) and CF<sub>3</sub>CH<sub>2</sub>Br at 1082.3 cm<sup>-1</sup> ( $\bigtriangleup$ ). The value on the  $\phi \approx 0$  line is  $\sigma_0$ .

sensitized reaction in the presence of toluene. The relative importance of the product channels with toluene is the same as that for the direct reactions. The ratios of  $CF_2$ =CHCl/CF<sub>2</sub>=CHF and  $CF_2$ =CHCl/CF<sub>2</sub>=CH<sub>2</sub> vs.  $\phi$  are plotted in Figure 5 with the approximate temperatures designated for various fluences. The temperatures were calculated as described in Appendix II.

III. Absorbed Laser Energy and Cross Section Measurements. The values of  $\sigma_{\rm L}(\phi)$  vs.  $\phi$  determined at 1084.6 and 1092.0 cm<sup>-1</sup> for CF<sub>3</sub>CH<sub>2</sub>Cl are shown in Figure 6. Also depicted are the  $\sigma_1(\phi)$ values for CF<sub>3</sub>CH<sub>3</sub> and CF<sub>3</sub>CH<sub>2</sub>Br. The  $\sigma_{L}(\phi)$  for CF<sub>3</sub>CH<sub>2</sub>Br was determined from Beer's law plots.9 The values plotted for CF<sub>3</sub>CH<sub>3</sub> are actually the measured cross sections extrapolated to zero pressure, since the cross sections were pressure dependent.<sup>9</sup> For CF<sub>3</sub>CH<sub>2</sub>Cl the cross sections were independent of pressure (0.5-5 torr) for  $\phi \ge 0.5 \text{ J/cm}^2$ . For lower fluence the cross sections appeared to have a weak pressure dependence; however, the dependence was only slightly larger than the experimental uncertainty. The  $\sigma_1(\phi)$  for "large" CF<sub>3</sub>CH<sub>2</sub>Br extrapolates to the conventional broad-band cross section,  $\sigma_0$ , as  $\phi$  approaches zero. In contrast,  $\sigma_0$  and  $\sigma_L(\phi)$  do not coincide for "small" CF<sub>3</sub>CH<sub>3</sub>. Even at  $\phi = 0.02 \text{ J/cm}^2$ ,  $\sigma_L(\phi) = 2.0 \times 10^{-19} \text{ cm}^2/\text{molecule}$ , which is less than half of the broad-band cross section of  $4.6 \times 10^{-19}$ cm<sup>2</sup>/molecule.

At 1084.6 cm<sup>-1</sup>  $\sigma_0$  and  $\sigma_L(\phi)$  do not coincide for CF<sub>3</sub>CH<sub>2</sub>Cl; however, the difference is not as pronounced as for CF<sub>3</sub>CH<sub>2</sub>. Since CF<sub>3</sub>CH<sub>2</sub>Cl has a larger  $\sigma_0$  (2.3 × 10<sup>-19</sup> cm<sup>2</sup>/molecule) at 1092.0 cm<sup>-1</sup> than at 1084.6 cm<sup>-1</sup> (9.4 × 10<sup>-20</sup> cm<sup>2</sup>/molecule) because the former is closer to the maximum in the absorption band, more low  $\phi$  measurements were done at this frequency. However, no enhancement in  $\sigma_L(\phi)$  was observed even down to  $\phi = 0.06$  J/cm<sup>2</sup> and the discrepancy in  $\sigma_0$  and  $\sigma_L(\phi)$  for 1092.0 cm<sup>-1</sup> is about a factor of 2. The CF<sub>3</sub>CH<sub>2</sub>Cl band has a half-width of ~25 cm<sup>-1</sup> and some rotational structure<sup>14</sup> does appear around the band maximum (1110 cm<sup>-1</sup>) for a resolution of 0.03 cm<sup>-1</sup>. Both 1084.6 and 1092.0 cm<sup>-1</sup> are to the red side of the half-width position and no rotational structure is evident.

Plots of the reaction probability vs. the average absorbed energy  $P(\langle E \rangle)$ , inherently should be more informative than  $P(\phi)$  vs.  $\phi$ , since the extent of reaction is directly related to the absorbed energy. With the availability of the  $\sigma_L(\phi)$  values such graphs for CF<sub>3</sub>CH<sub>3</sub>, CF<sub>3</sub>CH<sub>2</sub>Cl, and CF<sub>3</sub>CH<sub>2</sub>Br can be constructed. If all molecules absorb the energy, the average energy absorbed per molecule in the irradiated volume,  $\langle E \rangle$ , is given by  $\langle E \rangle = \phi \times \sigma_L(\phi)$ . Plots of  $P(\langle E \rangle)$  vs.  $\langle E \rangle$  for CF<sub>3</sub>CH<sub>2</sub>Cl, CF<sub>3</sub>CH<sub>3</sub>, and CF<sub>3</sub>CH<sub>2</sub>Br are given in Figure 7. The data for CF<sub>3</sub>CH<sub>3</sub> and CF<sub>3</sub>CH<sub>2</sub>Br were taken from ref 9; however, both the  $P(\phi)$  and  $\sigma_L(\phi)$  results for CF<sub>3</sub>CH<sub>2</sub>Br were checked and confirmed in the present study.<sup>14</sup> The switch in positions of the curves for CF<sub>3</sub>CH<sub>3</sub>CH<sub>3</sub>Br in Figure 7 relative to Figure 1 should be noted. This emphasizes the importance of  $\sigma_L(\phi)$  measurements in modeling laser-induced reactions.



Figure 7. Reaction probability,  $P(\langle E \rangle)$ , vs. average absorbed energy,  $\langle E \rangle$ , for CF<sub>3</sub>CH<sub>3</sub>, CF<sub>3</sub>CH<sub>2</sub>Cl, and CF<sub>3</sub>CH<sub>2</sub>Br.

TABLE I: RRKM Grouped Frequencies (cm<sup>-1</sup>), Reaction Path Degeneracies, Ratios of Moment of Inertia, Estimated  $E_0$  and log A Values, and  $\Delta H^{\circ}_{298}$  for Reactions 1-3

	transition states		
CF <sub>3</sub> CH <sub>2</sub> Cl	HF elim	HCl elim	C-Cl homolysis
3019 (2)	2999 (1)	3044 (1)	3019 (2)
1261 (6)	1200 (3)	1400 (2)	1266 (6)
853 (3)	1134 (1)	1201 (4)	880 (2)
572 (3)	700 (2)	864 (4)	574 (3)
342 (2)	550 (2)	541 (2)	355 (1)
180 (1)	500 (1)	310 (2)	75 (2)
109 (1)	145 (2)	100 (2)	45 (1)
degeneracy	4	2	1
$(I^+/I)^{1/2}$	1.00	1.04	2.00
$\log A$ , s <sup>-1</sup>	13.8	13.8	14.8
$E_0$ , kcal/mol	76	80	83
$\Delta H^{\circ}_{298}$ , kcal/mol	33.7	40.1	82.8

#### Discussion

I. Unimolecular Reaction Channels. The enthalpies of reaction and the estimated preexponential and threshold energy values for the three channels are summarized at the bottom of Table I. The preexponential factor for the C-Cl rupture channel is the least reliable of the estimates.

The four-centered,  $\alpha,\beta$ -elimination (reaction 1) and threecentered,  $\alpha,\alpha$ -elimination (reaction 2) processes are well-documented for halogenated ethanes. The  $\alpha,\beta$ -elimination reaction proceeds by a simultaneous breaking of the C-F and C-H bonds and formation of the C=C double bond and the H-F bond (hence, four-centered) and leads directly to stable products. The  $\alpha,\alpha$ elimination reaction proceeds by the concerted breaking of the C-H and C-Cl bonds with formation of the H-Cl bond (hence, three-centered) and produces a carbene intermediate. The intramolecular rearrangement of CF<sub>3</sub>CH to CF<sub>2</sub>=CHF by F migration has been studied by Haszeldine and co-workers<sup>16</sup> and more recently by Holmes.<sup>13</sup> In our work CF<sub>3</sub>CH is apparently formed with sufficient internal energy that the small threshold energy for rearrangement does not inhibit the F migration.

Reaction 3, C–Cl bond homolysis, is expected to be much more competitive than any other homolytic processes based on the estimated bond energies (kcal mol<sup>-1</sup>) in CF<sub>3</sub>CH<sub>2</sub>Cl:<sup>17</sup> C–F ( $\sim$  108) > C–C ( $\sim$ 100) > C–H ( $\sim$ 98) > C–Cl ( $\sim$ 83). Rupture of C–Cl has been suggested as a reaction pathway at temperatures above 1270 K in shock tube experiments.<sup>12</sup> The intermediate

<sup>(15)</sup> W. Tsang, J. Phys. Chem., 88, 2812 (1984).

<sup>(16)</sup> R. Fields and R. N. Haszeldine, J. Chem. Soc., 1881 (1964); J. H. Atherton, R. Fields, and R. N. Haszeldine, J. Chem. Soc. C, 366 (1971).

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Figure 8. Experimental and calculated ratios of  $CF_2$ — $CHCl/CF_2$ — $CH_2$  vs. 1/T for SiF<sub>4</sub>-sensitized reaction of CF<sub>3</sub>CH<sub>2</sub>Cl; the calculations are based upon the Arrhenius parameters of Table I.

CF<sub>3</sub>CH<sub>2</sub> radical can be expected to react by  $\beta$ -elimination of F to produce CF<sub>2</sub>=CH<sub>2</sub>, as observed in the present study. The ethyl radical, CH<sub>3</sub>CH<sub>2</sub>, is known to react via  $\beta$ -elimination of H with a threshold energy ~2 kcal/mol higher than the reaction endothermicity. Tsang has estimated an activation energy on the order of ~18 kcal/mol for the  $\beta$ -elimination of Br from CF<sub>2</sub>CF<sub>2</sub>Br.<sup>15</sup> If similar energetics apply to CF<sub>3</sub>CH<sub>2</sub>,  $\beta$ -elimination of F should occur with a threshold energy of ~29 kcal/mol. In sensitization reactions the temperature in the irradiation zone is very high, and the CF<sub>3</sub>CH<sub>2</sub> radicals will form CF<sub>2</sub>CH<sub>2</sub> + F. In the direct laser-induced reaction, the CF<sub>3</sub>CH<sub>2</sub> formed from C-Cl rupture may continue to absorb laser energy and F atom rupture will follow even if CF<sub>3</sub>CH<sub>2</sub> initially lacks enough energy to react.<sup>18</sup>

The fate of the F and Cl atoms produced by the C-Cl rupture channel (reaction 3) was considered in some detail.<sup>14</sup> For direct laser photolysis the experiments employing toluene as a free-radical scavenger (Figure 3) indicated no effect of toluene concentration, and it was concluded that reaction of the F and Cl atoms with the reaction cell walls most likely occurs for the low-pressure direct irradiation experiments. The data of Figure 4 indicate, however, that secondary reactions are important in the SiF<sub>4</sub>-sensitized experiments, and that CF<sub>2</sub>=CHF is formed in significant amounts at the expense of CF<sub>2</sub>=CHCl in the absence of toluene. It is suggested that reaction 4 accounts for these observations.

$$CF_2 = CHCl + F \rightarrow [CF_2 - CHFCl]^* \rightarrow CF_2 = CHF + Cl$$
(4)

Examination<sup>14</sup> of literature values for Arrhenius parameters for a number of four-centered  $\alpha,\beta$ -elimination reactions suggests log  $A \sim 13.2$  per reaction channel, which translates into log  $A \sim 13.8$  for CF<sub>3</sub>CH<sub>2</sub>Cl with a reaction path degeneracy of four. This value agrees with that determined by Holmes<sup>13</sup> obtained by matching observed and calculated chemical activation rate constants. Both the  $E_0$  (67.6 kcal/mol) and log A (12.7 s<sup>-1</sup>) values from the shock tube data<sup>12</sup> appear too low and we have assumed Holmes' model to be more reliable and have utilized these values in the present work (Table I).

A similar examination<sup>14</sup> of literature values for three-centered,  $\alpha, \alpha$ -eliminations of HCl indicated that  $E_0$  is generally 2-3 kcal/mol higher than for a four-centered elimination<sup>19</sup> and that  $A \sim 13.5$  per reaction channel. We arrive at the values listed in Table I from the experimental results for CF<sub>3</sub>CH<sub>2</sub>Cl discussed below. Again, the values from the shock tube experiments<sup>12</sup> appear too low.

A reasonable estimate<sup>17</sup> for the preexponential factor for C-Cl band homolysis is 10<sup>15.0</sup> and the threshold energy will be equal to the bond dissociation energy. The value used for the preexponential factor for reaction 3 was selected from consideration of the results from the sensitized reactions. If the temperature was known, the difference in activation energies could be assigned from an Arrhenius-type plot, Figure 8. In principle, the temperature can be determined from laser energy absorption measurements, i.e.,  $\langle E \rangle = \int_{298}^{T} C_p \, dT$  in which  $C_p$  is the heat capacity of SiF<sub>4</sub>.<sup>20</sup> Absorption measurements for 5.0 torr of SiF<sub>4</sub> at 1027.4 cm<sup>-1</sup> were performed as described in Appendix II and the temperature was calculated. The effective temperatures produced in the irradiated volume at different fluences were assigned as indicated in Figure 5. It is unlikely that inverse electronic relaxation of vibrationally excited SiF4 into an electronic state of SiF<sub>4</sub> followed by electronic energy transfer to CF<sub>3</sub>CH<sub>2</sub>Cl occurs. Such an effect was demonstrated by Kramer for the SiF<sub>4</sub>-sensitized reaction of  $CF_2HCl$  but only by utilizing laser fluences > 25  $M/cm^{2,21}$  Moore et al<sup>22</sup> have also assigned temperatures for SiF<sub>4</sub>-sensitized reactions utilizing a transport property model. Agreement between the present method (see Appendix II) and the approach of Moore et  $al^{22}$  is reasonably good for T < 1350K; above this temperature our method gives higher temperatures.

A comparison of the experimental CF<sub>2</sub>=CHCl/CF<sub>2</sub>=CH<sub>2</sub> ratio (HF elimination vs. C-Cl homolysis) for the SiF4-sensitized reaction with the ratio calculated from the temperature and transition-state models is given by Figure 8. If the calculated and experiment values are parallel then the difference in  $\Delta E_0$  and in the models is satisfactory. Figure 8 suggests that  $E_0(C-$ Cl)- $E_0(HF) = 7$  kcal mol<sup>-1</sup> is a reasonable estimate. A similar plot for CF<sub>2</sub>=CHCl/CF<sub>2</sub>=CHF is somewhat less satisfactory for an energy difference of 4 kcal mol<sup>-1</sup> for  $E_0(\text{HCl}) - E_0(\text{HF})$ . Since the assignment for the  $\log A$  value for reaction 3 is no better than  $\pm 0.5$ , the agreement in Figure 8 is acceptable. If  $E_0(HF)$ is accepted from Holmes work then  $E_0(C-Cl) = 83$  and  $E_0(HCl)$ = 80 kcal mol<sup>-1</sup>, based upon the results of the sensitized experiments. Although the temperature assignments are not extremely reliable, they are sufficient to indicate the magnitude of the activation energy differences.

II. Multiphoton Laser-Induced Reaction Dynamics. There are three lines of evidence indicating that significant fractionation of molecules occurs as a result of laser energy absorption, i.e., not all of the molecules within the irradiated volume actually absorb the same average energy. As a consequence, a two-component energy distribution is produced in which a certain fraction of molecules absorb energy and become highly excited while the remaining molecules are not excited or only weakly excited.

1. Reaction Probability vs. Absorbed Energy. In comparing  $P(\phi)$  of CF<sub>3</sub>CH<sub>2</sub>Br, CF<sub>3</sub>CH<sub>2</sub>Cl, and CF<sub>3</sub>CH<sub>3</sub> at the same  $\phi$ (Figure 1), CF<sub>3</sub>CH<sub>2</sub>Br had the highest extent of reaction and  $CF_3CH_3$  the lowest for a given  $\phi$ . But, if the reaction probabilities vs. absorbed laser energy, Figure 7, are compared, these three reactions appear in a different way and CF<sub>3</sub>CH<sub>3</sub> shows more reaction compared to CF<sub>3</sub>CH<sub>2</sub>Br. The simplest explanation is that only a fraction of the CF<sub>3</sub>CH<sub>3</sub> molecules in the irradiated volume actually absorbs the laser energy. If so, a two-component distribution of molecules is produced after laser excitation and the fraction absorbing energy will have a much higher mean energy than predicted by the  $\langle E \rangle$  calculated assuming all molecules absorb the energy. The highly activated molecules have high  $k_{\rm F}$ values and react more readily. The fraction that absorbs the energy probably is fluence dependent, i.e., becomes larger at higher fluence. The degree of fractionation declines in the CF<sub>3</sub>CH<sub>3</sub>, CF<sub>3</sub>CH<sub>2</sub>Cl, CH<sub>3</sub>CH<sub>2</sub>Br series. However, some fractionation apparently still exists for  $CF_3CH_2Br$  since  $P(\phi)$  approaches 0.5

<sup>(18)</sup> For examples of such multiphoton-induced secondary reactions see: J. S. Francisco, M. A. Findeis, and J. I. Steinfeld, *Int. J. Chem. Kinet.*, **13**, 627 (1981); F. Zhang, J. S. Francisco, and J. I. Steinfeld, *J. Phys. Chem.*, **86**, 2402 (1982).

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**Figure 9.** Comparison of the experimentally measured mean energy  $\langle E \rangle$  (lower scale) and the  $\langle E \rangle$  (upper scale) required for the same RRKM calculated percent HF elimination. The large difference shows that the molecules undergoing unimolecular reactions have more energy than calculated assuming all molecules absorb the laser energy.

rather than unity. Some reservation should be maintained about absolute  $P(\phi)$  values because the irradiated volume becomes difficult to measure if focused conditions are used. Nevertheless,  $P(\phi) = 0.5$  seems to be sufficiently different from 1.0 to be significant. A situation closely resembling this one is the comparison for CF<sub>3</sub>I and CF<sub>3</sub>CFICF<sub>3</sub> in which the larger molecule had the lower  $P(\phi)$  as  $\phi$  approached the saturation regime.<sup>10</sup>

The CF<sub>3</sub>CH<sub>3</sub> example is particularly clear-cut; it is a "small" molecule as discussed earlier. The threshold energy for HF elimination from CF<sub>3</sub>CH<sub>3</sub> is 68 kcal/mol; from Figure 7, 20% reaction occurs at  $\langle E \rangle \sim 23$  kcal/mol. This energy is much lower than the threshold energy, and there must necessarily be fractionation. If only  $^{1}/_{4}$  of the molecules absorb laser energy, one can explain the 20% reaction; i.e., essentially all the molecules that, in fact, absorb the energy do react, since  $\langle E \rangle \sim 100$  kcal/mol for the fraction that participates in the absorption process. On the other hand,  $P(\phi) \approx 0.4$  at  $\phi = 2.5$  J/cm<sup>2</sup> for which  $\langle E \rangle = 96$  kcal mol<sup>-1</sup> for CF<sub>3</sub>CH<sub>2</sub>Br, a "large" molecule, and no fractionation is required based on the  $\langle E \rangle$  argument. All the molecules within the irradiated zone may absorb the laser energy. However, since  $P(\phi)$  tends to a constant value less than unity there still may be some fractionation.

2. Comparison of Product Distribution and RRKM Rate Constants. A comparison of the experimental and calculated RRKM  $[k_{\rm HF}/(k_{\rm HF} + k_{\rm HCl} + k_{\rm C-Cl})]$  percentage of HF elimination from CF<sub>3</sub> CH<sub>2</sub>Cl vs. the experimental and calculated  $\langle E \rangle$  values is shown in Figure 9. Since the  $\langle E \rangle$  values derived from the absorption measurements are lower than the  $\langle E \rangle$  values needed to match the yield fractions, two different  $\langle E \rangle$  scales are provided in Figure 9. An experimental HF-elimination fraction of 0.85 corresponds to an experimental  $\langle E \rangle \sim 10$  kcal/mol. For this same fraction the ratio of rate constants give  $\langle E \rangle \sim 85$  kcal/mol, suggesting a fractionation of  $\sim 1/9$ . For an HF-elimination fraction of 0.5, the experimental  $\langle E \rangle$  is ~40 kcal/mol and the rate constant  $\langle E \rangle \sim 105$  kcal/mol indicating a  $1/2^{-1}/3$  fractionation. Even for a fraction of 0.3, the experimental  $\langle E \rangle$  is ~67 kcal/mol vs.  $\sim$ 120 kcal/mol for the rate constant ratio, suggesting a fractionation of  $\sim 1/2$ . A comparison of the ratios for the other channels would show a similar shift in the energy scales. In particular,  $k_{\rm E}({\rm HF}) \approx k_{\rm E}({\rm C-Cl})$  at  $\langle E \rangle \approx 100$  kcal mol<sup>-1</sup>. Although the experimental error limits for the laser fluence, irradiation zone, absorption measurements, and reaction probability all increase at high  $\phi$ , the trend is unmistakable. There is severe fractionation at low fluences for CF<sub>3</sub>CH<sub>2</sub>Cl that diminishes, but is not eliminated, as the fluence is increased.

TABLE II: Absorption Data for 5.0 torr of  $SiF_4$  in a 3.0 cm Length Cell Irradiated at 1027.4 cm<sup>-1</sup>

$\phi$ , J/cm <sup>2</sup>	pulse energy, J	$\sigma_{\rm L}(\phi) \times 10^{-19},$ cm <sup>2</sup> /molecule	absorbed energy, kcal/mol	<i>Т</i> , К
0.19	0.08	5.5	14.3	946
0.22	0.10	5.1	16.3	1010
0.36	0.13	4.9	19.8	1175
0.43	0.16	4.8	25.0	1380
0.47	0.22	4.5	29.5	1558
0.59	0.26	4.3	34.2	1744

Further evidence for fractionation of absorbed energy in the laser-induced reaction of CF<sub>3</sub>CH<sub>2</sub>Cl can be obtained from an analysis of the quenching effect of added toluene. On the strong-collision assumption, the first-order rate constant for quenching is equal to the collision frequency; i.e., every collision of a vibrationally excited CF<sub>3</sub>CH<sub>2</sub>Cl with a molecule of toluene deactivates the CF<sub>3</sub>CH<sub>2</sub>Cl and prevents unimolecular reaction. The collision frequency,  $k_{\rm E}$ , is given by  $k_{\rm E} = zP$  in which P is the total pressure and z is the collision number. An estimate of  $\langle E \rangle$ can be made by equating  $k_{(E)}$  with the collision number for the half-quenching pressure of toluene.<sup>23</sup> From the data in Figure 3,  $P_{1/2} = 1.2$  torr for  $\phi = 3.4$  J/cm<sup>2</sup> and  $P_{1/2} = 0.06$  torr for  $\phi = 1.6$  J/cm<sup>2</sup>.<sup>14</sup> The  $k_E$  values calculated for these pressures are  $\sim 5 \times 10^7$  and  $\sim 3 \times 10^6$  s<sup>-1</sup>, respectively. These  $k_{\langle E \rangle}$  values correspond to  $\langle E \rangle$  values of 105 and 95 kcal/mol, respectively. In contrast, the  $\langle E \rangle$  based on energy absorption for  $\phi = 3.4$  and 1.6 J/cm<sup>2</sup> are only 45 and 15 kcal/mol, respectively. These  $\langle E \rangle$ values closely match the  $\langle E \rangle$  from the product ratios indicating a significant fractionation of absorbed laser energy.

### Conclusion

The infrared multiphoton laser-induced reaction of  $CF_3CH_2Cl$ , a compound with three reaction channels, provides insight into the laser-driven unimolecular reactions of halogenated ethanes. This compound appears to be in the transition regime between "small" and "large" molecules. The following points were established.

(1) The laser energy absorption cross sections and reaction probabilities were measured from  $\phi = 0.1$  to 3.0 J/cm<sup>2</sup> at 1084.6 cm<sup>-1</sup>.

(2) The absolute reaction yields and the product channel ratios were very dependent on laser fluence. The maximum yield was  $P(\phi) = 0.8$ ; C-Cl homolysis was the main reaction channel at high fluence. This is another example in which a high  $E_0$ /high preexponential factor channel can be made to dominate over a low  $E_0$  channel.

(3) The addition of toluene reduced the absolute yield indicating that collisional quenching of excited molecules was competitive with reaction for toluene pressures > 0.05 torr at  $\phi = 1.6 \text{ J/cm}^2$  and > 0.8 torr at  $\phi = 3.4 \text{ J/cm}^2$ . However, the relative contribution for different reaction channels was not affected.

(4) The experimental yields and product ratios were measured for  $SiF_4$ -sensitized experiments. The yields and product ratios were consistent with expected values from the assigned temperatures and elementary rate constants for the three reaction channels.

(5) A conflict between the experimentally measured absorbed energy and the energy of the reacting molecules assigned from RRKM rate constants can only be resolved by assuming a significant fractionation in the laser excitation dynamics with the fraction of molecules actually absorbing energy being dependent on fluence.

(6) Such fractionation may be common in multiphoton excitation processes generating severely non-Boltzmann population distributions and complicating interpretations based on bulk laser cross sections that may be grossly different from microscopic cross



Figure 10. Temperature within irradiated volume for 5.0 torr of  $SiF_4$  at 1027.4 cm<sup>-1</sup> vs. incident laser fluence; this work (O); Moore et al.<sup>22</sup> ( $\bullet$ ).

sections.

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# Appendix I. RRKM Model for the Three Reaction Channels of CF<sub>3</sub>CH<sub>2</sub>Cl

The grouped frequencies,<sup>24</sup> reaction path degeneracies, ratios of moment of inertia of CF<sub>3</sub>CH<sub>2</sub>Cl, and transition states for the three reaction channels are listed in Table I.

## Appendix II. Laser Absorption Measurements and Temperature Assignments for SiF<sub>4</sub>-Sensitized Reactions

Laser energy absorption measurements for SiF<sub>4</sub> at 1027.4 cm<sup>-1</sup> were performed with 5.0 torr in a 3.0-cm length cell. The cross sections were dependent on SiF<sub>4</sub> pressure; i.e., the multiphoton absorption of SiF<sub>4</sub> does not follow Beer's law. The transmittance, cross sections, absorbed energy, and the temperature as assigned from the SiF<sub>4</sub> heat capacity<sup>20</sup> are shown in Table II. Estimated error limits for  $\sigma_L(\phi)$  are ±8% which corresponds to uncertainties in the temperature assignments of  $\pm 80$  °C.

In Moore's et al. work,<sup>22</sup> an internal iris of 8.0-mm diameter produced a multimode beam with a near-Gaussian profile. In our work, a constant fluence profile beam was used and the temperature will not be exactly comparable for the same absorbed energy. For ease of comparison between this work and Moore's et al.<sup>22</sup> results, we converted our  $\phi$  to laser energy as shown in Figure 10. For laser energies  $\leq 0.15$  J, the temperature assignments are similar, but significant differences exist for laser energies ≥0.15 J.

**Registry No.** CF<sub>3</sub>CH<sub>2</sub>Cl, 75-88-7.

(24) H. W. Chang, Ph.D. Thesis, Kansas State University, 1971.

# Dispersion-Induced Circular Dichroism Spectra of Benzophenone and Fluorenone in **Chiral Solutions**

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The induced circular dichroism spectra of the low energy absorption bands of benzophenone and fluorenone in a range of chiral media are presented. The results illustrate the essential difference between DICD (dispersion-induced circular dichroism) spectra of electric dipole allowed and magnetic dipole allowed transitions. The DICD of the benzophenone band is consistent with earlier assignments as a  ${}^{1}A_{1} \rightarrow {}^{1}A_{2}$  n  $\rightarrow \pi^{*}$  transition, but shows a clear vibrational progression in the carbonyl stretch based on the true band origin, and a more resolved blue shift in polar solvents. The DICD of the fluorenone band manifests a red shift in polar solvents, and suggests a reassignment of this band as comprising two separate  $\pi \rightarrow \pi^*$  transitions, a  ${}^{1}A_{1}$  $\rightarrow$  <sup>1</sup>B<sub>2</sub> at lower energy, with a <sup>1</sup>A<sub>1</sub>  $\rightarrow$  <sup>1</sup>A<sub>1</sub> at slightly shorter wavelengths. The former appears to result directly from the  $\pi$ -system of the rings, whereas the latter appears to be more localized on the carbonyl group.

# Introduction

The circular dichroism of the transitions of achiral molecules (A) interacting with chiral species (C) present in the same solution is referred to, in the limit of no orientational correlation between A and C, as DICD (dispersion-induced circular dichroism). The effect has been experimentally well established for a range of organic<sup>1-3</sup> and inorganic<sup>4,5</sup> chromophores. With the development of a theoretical DICD model,<sup>6,7</sup> it has been suggested that the effect could serve as a basis of a technique complementary to

normal absorption for the spectroscopic assignment of achiral species in solution. This initial speculation has recently been consolidated by an experimental study of the DICD of Co(III) complexes in sugar solutions.<sup>5</sup> In this paper, we apply the technique to two aromatic carbonyls, benzophenone and fluorenone

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