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INFRARED MULTIPHOTON DISSOCIATION OF  $\text{CF}_3\text{CHClF}$ :  
PRIMARY DISSOCIATION AND SECONDARY PHOTOLYSIS

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**Abstract** The dissociation yield and branching ratio in  $\text{CO}_2$  laser-induced infrared multiphoton dissociation (IRMPD) of  $\text{CF}_3\text{CHClF}$  were investigated by irradiation at  $9\text{R}(20)$   $1078.6\text{ cm}^{-1}$  under an unfocused irradiation geometry ( $0.75\text{--}2.3\text{ J/cm}^2$ ) and a mildly focused one ( $1.2\text{--}18\text{ J/cm}^2$ ). By using a  $\text{Br}_2$ -scavenging technique, it was revealed that the primary dissociation of  $\text{CF}_3\text{CHClF}$  proceeded mainly via three-centered  $\text{HCl}$  molecular elimination and C-Cl bond rupture, with minor contributions of C-C bond rupture and  $\text{HF}$  molecular elimination at higher fluences. The secondary photolysis of the primarily produced species during the laser pulse to yield  $\text{CF}_2$  and  $\text{CClF}$  carbenes depended strongly upon the laser fluence.

## INTRODUCTION

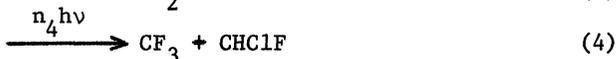
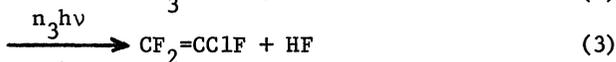
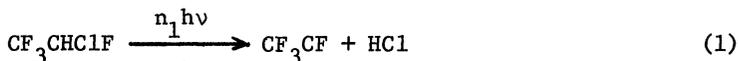
Multichannel dissociation of a large polyatomic molecule induced by absorption of pulsed infrared laser photons is a good probe to the molecular excitation and unimolecular dissociation mechanisms in the gas phase.<sup>1-2</sup> The branching ratio in primary dissociation pathways has been extensively studied as a function of experimental parameters such as irradiation frequency, laser fluence, intensity, and reactant pressure. It has been, however, often quite difficult to

reveal the IRMPD of large polyatomic molecules, since a large number of intermediate species produced via plural primary dissociation pathways make the final product distribution complicated. The secondary photolysis of primary species during the laser pulse further complicates the products. In a similar sense the real-time spectroscopic analysis cannot always be applicable to such complicated reaction systems.

We have recently reported the mechanisms in IRMPD of  $\text{CF}_3\text{CHF}_2$ <sup>3</sup> and  $\text{CF}_3\text{CF}_2\text{CHF}_2$ <sup>4</sup> where HF molecular elimination and C-C bond rupture(s) are possible. A radical scavenging technique with  $\text{Br}_2$  was successfully employed to distinguish the primary and secondary dissociation pathways in these molecules by precise determination of intermediate species as bromides. This technique revealed that the high-activation-energy C-C rupture channel(s) dominated over an HF elimination channel at a relatively low laser fluence, indicating that large polyatomic molecules subjected to a strong infrared laser field could be excited far beyond the lowest dissociation threshold. Also revealed was that the secondary photolysis of primarily produced radicals such as  $\text{CF}_3$  and  $\text{CHF}_2$  during the laser pulse took place efficiently depending strongly upon the laser fluence. The frequency dependence of the radical secondary photolysis was also studied in the IRMPD of  $\text{CF}_3\text{CF}_2\text{CHF}_2$ .<sup>4</sup> Although first demonstrated in the IRMPD of relatively small or simple molecules,<sup>5-6</sup> this technique was found to be most useful in IRMPD studies of large polyatomic molecules with complex dissociation pathways, such as  $\text{CF}_3\text{CHF}_2$  and  $\text{CF}_3\text{CF}_2\text{CHF}_2$ . The radical scavenging with  $\text{I}_2$  was also successfully employed to reveal the IRMPD of  $(\text{CF}_3)_3\text{CBr}$ .<sup>7</sup>

In this paper we report the IRMPD of 1,1,1,2-tetrafluoro-

chloroethane (CF<sub>3</sub>CHClF), which is one of the most promising working substances for the laser isotope separation (LIS) of tritium.<sup>8-9</sup> Although no mechanistic studies have been reported on the thermal decomposition of CF<sub>3</sub>CHClF, its dissociation scheme is considered more complicated than those for CF<sub>3</sub>CHF<sub>2</sub> and CF<sub>3</sub>CF<sub>2</sub>CHF<sub>2</sub>. Four primary dissociation pathways are possible in the IRMPD of CF<sub>3</sub>CHClF by analogy with the unimolecular dissociation mechanisms for such highly substituted halocarbons.<sup>10</sup>



The primary pathways and their branching ratios were investigated as a function of laser fluence by using Br<sub>2</sub> as a scavenger for these primary radicals and olefins. The SiF<sub>4</sub>-sensitized heating of a CF<sub>3</sub>CHClF/Br<sub>2</sub> mixture was also examined to evaluate the contribution of purely thermal reaction to this reaction system.

## EXPERIMENTAL

### Irradiation Sample

1,1,1,2-Tetrafluorochloroethane (CF<sub>3</sub>CHClF, b.p. -12°C, Daikin Kogyo Co. Ltd.) was purified to more than 99 % repeatedly by preparative gas chromatography to remove its isomer, CHF<sub>2</sub>CClF<sub>2</sub>. Bromine (Wako Pure Chemical, Ltd.) was degassed before use.

In the IRMPD experiments samples of CF<sub>3</sub>CHClF (100 mTorr) without or with a 50-fold excess (5 Torr) of Br<sub>2</sub> were irradiated. Upon addition of 5 Torr Br<sub>2</sub> as a scavenger, all the radicals produced were completely scavenged to yield bromides

without recombination of the nascent radicals. The conversion of  $\text{CF}_3\text{CHClF}$  was always kept below 10 %. In this conversion range, the photolysis of scavenged bromides was virtually negligible.

#### Laser and Irradiation Geometry

A TEA  $\text{CO}_2$  laser (Lumonics 103-2) with a lasing gas of He and  $\text{CO}_2$  ( $\approx 100$ -ns pulse duration) was used for multiphoton excitation of  $\text{CF}_3\text{CHClF}$ . Irradiation line used was 9R(20)  $1078.6\text{ cm}^{-1}$  corresponding to the red-side wing of a strong IR peak at about  $1100\text{ cm}^{-1}$  (Figure 1).

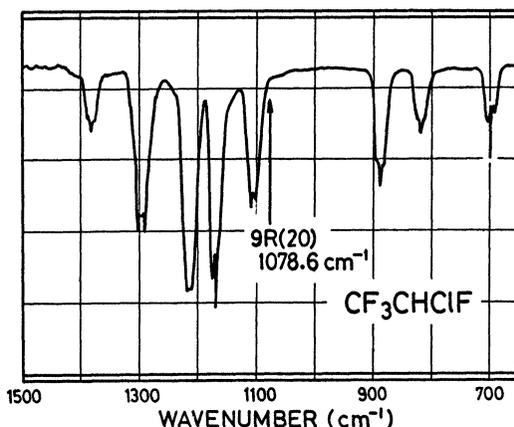


FIGURE 1. IR absorption spectrum of  $\text{CF}_3\text{CHClF}$  and an irradiation line. Sample pressure: 5 Torr; cell length: 5 cm.

The transverse intensity profile was measured by scanning a pinhole (1 mm in diameter) and observing the intensity profile with a pyroelectric detector; the profile was found to be nearly uniform. Laser pulses at a 0.5-Hz repetition rate were attenuated with  $\text{CaF}_2$  and/or  $\text{BaF}_2$  flats, passed through an aperture (14 mm in diameter), and then focused with  $\text{BaF}_2$  lenses.

Two types of irradiation geometry were employed in the IRMPD experiments: In the "unfocused" irradiation geometry, a Pyrex cell (2 cm i.d.; 30 cm in length) equipped with KCl optical windows was placed at the focal point of a  $\text{BaF}_2$  lens (f.l., 180 cm). The laser fluences at the entrance and at the center of the irradiation cell were found to differ by only 4 % or less; therefore, the laser beam was regarded as virtually uniform along the cell axis in this irradiation geometry.

When irradiation was performed at fluences higher than the damage threshold of the cell windows, a "mildly focused" irradiation geometry was adopted by using a  $\text{BaF}_2$  lens (f.l., 52 cm) to focus a laser beam mildly into the center of a long irradiation cell (2 cm i.d., 65 cm in length). The spot size of the laser beam was found to be about 3.5 mrad (full angle). Under the above irradiation conditions, the attenuation of a laser beam by the sample gas was virtually negligible.

#### Sensitization Experiments

In the sensitization experiments,  $\text{SiF}_4$  (5-10 Torr, PCR Inc.) was added to a  $\text{CF}_3\text{CHClF}$  (0.5 Torr)/ $\text{Br}_2$  (10 Torr) mixture. A laser line at  $9\text{P}(34)$   $1033.5 \text{ cm}^{-1}$  was used for irradiation at near the IR peak of  $\text{SiF}_4$ , where  $\text{CF}_3\text{CHClF}$  was nearly transparent. The sample gas was sealed in a short cell (2 cm i.d.; 10 cm in length) and irradiated with a nearly parallel beam at around the focal point of a  $\text{BaF}_2$  lens (f.l., 165 cm). The attenuation of the laser beam by the sample gas was 20-40 % depending upon the experimental conditions. The absorbed energy was measured from optical transmission through the cell.

#### Analysis

The irradiated sample was analyzed in a way similar to that

reported in Ref. 4. After removing  $\text{Br}_2$  with a precolumn containing anhydrous potassium ferrocyanide, the sample gas was injected into a gas chromatograph equipped with a Porapak-Q separation column (5 mm i.d.; 1 m or 3 m in length) and a thermal conductivity detector (TCD). The GC/MS and IR measurements were also employed for identification of irradiation products.

## RESULTS

### Dissociation Yield

The dissociation rate constant (  $d$  ) in IRMPD is defined by

$$d = -(1/t)\ln(1-X) \quad (6)$$

where  $X$  is the dissociated fraction of  $\text{CF}_3\text{CHClF}$  after irradiation by  $t$  pulses. In the unfocused irradiation geometry, the dissociation probability per pulse (  $q$  ) is obtained from the  $d$  value as

$$q = d V_c / V_{\text{irr}} \quad (7)$$

where  $V_c$  and  $V_{\text{irr}}$  are the volumes of a cell and an irradiation zone, respectively.

Figure 2 shows the fluence (  $\phi$  ) dependence of the dissociation probability (  $q$  ) in unfocused irradiation. The  $q$  values were found to depend strongly upon the laser fluence. The slope of a  $\log q$  vs.  $\log \phi$  plot ranged from 9 to 5 with an increase in fluence from 0.75 to 2.3  $\text{J}/\text{cm}^2$ . The dissociation rate constant (  $d$  ) determined for  $\text{CF}_3\text{CHClF}$  in a mildly focused irradiation is shown in Figure 3 as a function of pulse energy (  $E_0$  ) or focal fluence (  $\phi_f$  ) at the same irradiation frequency. The slope of the  $\log d$  vs.  $\log E_0$  plot in Figure 3 was about 5 in the  $E_0$  region lower than 0.06 J ( $\leq 2 \text{ J}/\text{cm}^2$  in  $\phi_f$ ); the obtained value is in agreement with

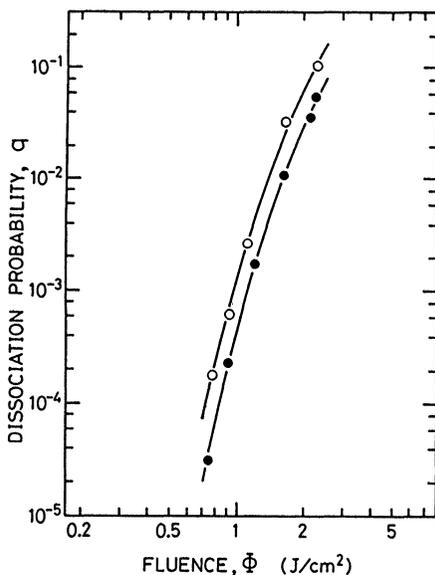


FIGURE 2. Dissociation probability ( $q$ ) for CF<sub>3</sub>CHClF as a function of laser fluence ( $\Phi$ ). Laser line: 9R (20) 1078.6 cm<sup>-1</sup>; sample: 100 mTorr of CF<sub>3</sub>CHClF without Br<sub>2</sub> (○) and with 5 Torr of Br<sub>2</sub> (●).

that observed in the same fluence region as in Figure 2. This indicates that in this low  $E_0$  region the dissociation of CF<sub>3</sub>CHClF occurred mainly within the Rayleigh range where the fluence was nearly uniform. Thus, the observed product distribution will reflect the intrinsic fluence dependence in this region. Above 0.06 J, on the other hand, the slope was found to decrease toward 1.5; this is a pure geometrical effect also observed in previous studies.<sup>3-4</sup> The product distribution will still depend upon the pulse energy in this geometrically biased region, since the condition  $d \propto E_0^{1.5}$  typical of a tightly focused geometry<sup>11-12</sup> was not fully met.

Figures 2 and 3 show that the addition of Br<sub>2</sub> brought

about a slight decrease in dissociation efficiency; this is presumably due to the collisional deexcitation as observed in the IRMPD of  $\text{CF}_3\text{CHF}_2$ <sup>3</sup> and  $\text{CF}_3\text{CF}_2\text{CHF}_2$ .<sup>4</sup> The extent of deexcitation, however, was too small to affect the discussion significantly as will be presented later.

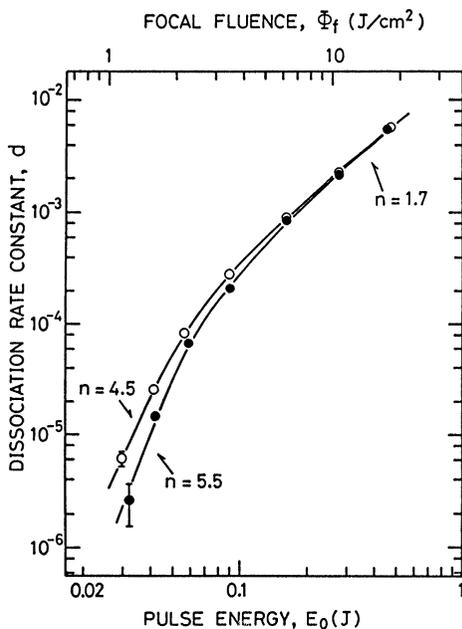


FIGURE 3. Dissociation rate constant ( $d$ ) for  $\text{CF}_3\text{-CHClF}$  as a function of pulse energy ( $E_0$ ) or focal fluence ( $\Phi_f$ ) in the mildly focused irradiation. Laser line: 9R(20) 1078.6  $\text{cm}^{-1}$ ; focal length of the lens: 52 cm; cell volume: 239  $\text{cm}^3$ ; sample: 100 mTorr of  $\text{CF}_3\text{CHClF}$  without  $\text{Br}_2$  (○) and with 5 Torr of  $\text{Br}_2$  (●).  $n$  is the slope of a  $\log d$  vs.  $\log E_0$  plot.

#### Products Scavenged by $\text{Br}_2$

The scavenged products found in the unfocused irradiation were  $\text{C}_2\text{Br}_2\text{F}_4$ ,  $\text{CF}_3\text{CHBrF}$ ,  $\text{CBrF}_3$ ,  $\text{CHBrClF}$ ,  $\text{CHBrF}_2$ , and  $\text{CBr}_2\text{F}_2$ . The IR analysis of  $\text{C}_2\text{Br}_2\text{F}_4$  discriminated from other products with a preparative GC revealed its structure as  $\text{CF}_3\text{CBr}_2\text{F}$

(1,1,1,2-tetrafluorodibromoethane). Under the mildly focused irradiation geometry,  $\text{CBrF}_2\text{CBrClF}$  and  $\text{CBr}_2\text{ClF}$  appeared in addition to the products listed above. A GC/MS analysis also revealed a minor product,  $\text{CBr}_3\text{F}$ , the determination of which was impossible due to its low yield. The carbon mass balance was found always satisfactory ( $\approx 100\%$ ).

Figure 4 shows the relative yields of the products observed in the unfocused irradiation as a function of laser fluence ( $0.75\text{--}2.3\text{ J/cm}^2$ ).

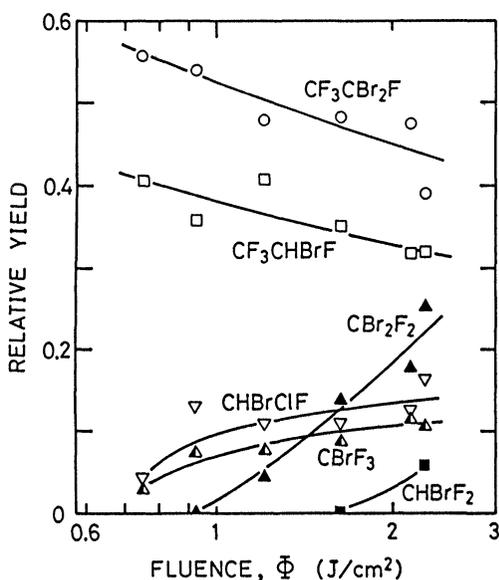
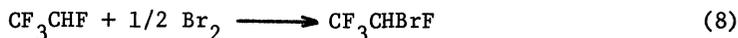
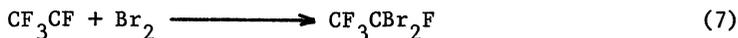


FIGURE 4. Laser fluence ( $\Phi$ ) dependence of relative yields of irradiation products. The relative yield was defined as the ratio of the pressure of the product to the consumed pressure of  $\text{CF}_3\text{CHClF}$ . Laser line:  $9\text{R}(20)\ 1078.6\text{ cm}^{-1}$ ; sample:  $100\text{ mTorr}$  of  $\text{CF}_3\text{CHClF}$  containing  $5\text{ Torr}$  of  $\text{Br}_2$ .

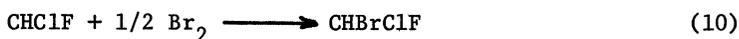
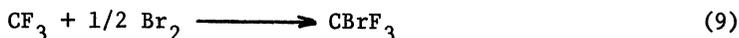
The major products were  $\text{CF}_3\text{CBr}_2\text{F}$  and  $\text{CF}_3\text{CHBrF}$ , which can be the scavenged products of  $\text{CF}_3\text{CF}$  carbenes and  $\text{CF}_3\text{CHF}$  radicals

originating from Eq. (1) and Eq. (2), respectively.



These scavenged products strongly suggest that the lowest activation energy channels in the unimolecular dissociation of  $\text{CF}_3\text{CHClF}$  are three-centered HCl molecular elimination and C-Cl bond rupture.

The relative yields of these products gradually decreased with an increase in fluence, accompanied by gradual increase in  $\text{CBrF}_3$  and  $\text{CHBrClF}$  yields. These bromides can be the scavenged products of  $\text{CF}_3$  and  $\text{CHClF}$  radicals originating from C-C bond rupture in Eq. (4).



The increase in  $\text{CBrF}_3$  and  $\text{CHBrClF}$  yields suggests that the contribution of C-C bond rupture channel increases at higher degrees of excitation.

At fluences above  $1 \text{ J/cm}^2$  a remarkable increase was observed in the relative yield of  $\text{CBr}_2\text{F}_2$ , the scavenged product of  $\text{CF}_2$  carbenes, the origin of which cannot be accounted for by the primary dissociation pathways presented in Eq. (1)-(4). A very small amount of  $\text{CHBrF}_2$ , the scavenged product of  $\text{CHF}_2$  radicals, was also observed at the highest fluence ( $2.3 \text{ J/cm}^2$ ) in Figure 4.

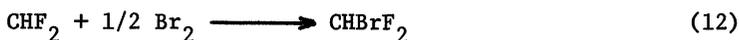
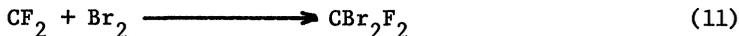


Figure 5 shows the scavenged products observed in a mildly focused irradiation as a function of pulse energy. The focal fluence ranged from  $1.2$  to  $18 \text{ J/cm}^2$ .

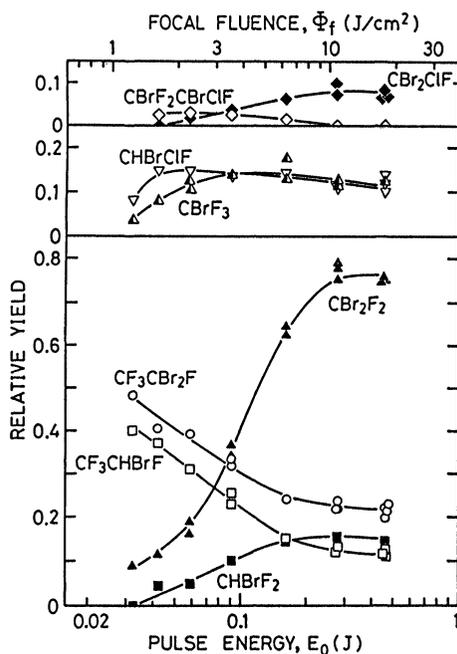
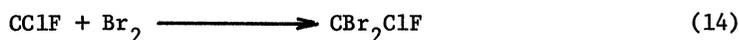
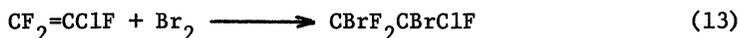


FIGURE 5. Dependence of relative yields of irradiation products upon pulse energy ( $E_0$ ) or focal fluence ( $\Phi_f$ ) in the mildly focused irradiation. The relative yield<sup>7</sup> was defined as in Figure 4. Laser line: 9R(20)  $1078.6 \text{ cm}^{-1}$ ; focal length of the lens: 52 cm; sample: 100 mTorr of  $\text{CF}_3\text{CHClF}$  containing 5 Torr of  $\text{Br}_2$ .

At  $E_0$  below  $0.06 \text{ J}$  ( $< 2.3 \text{ J/cm}^2$  in focal fluence), the product distribution was similar to that observed in the unfocused irradiation (Figure 4); this corresponds to the result that dissociation of  $\text{CF}_3\text{CHClF}$  occurred within the focal volume where the laser fluence was nearly uniform as mentioned previously. With an increase in focal fluence beyond  $2.3 \text{ J/cm}^2$ , the yields of  $\text{CF}_3\text{CBr}_2\text{F}$  and  $\text{CF}_3\text{CHBrF}$  decreased and those of  $\text{CBr}_2\text{F}_2$  and  $\text{CHBrF}_2$  increased (shown in the lower part of Figure 5). This trend is just what can be expected from the

data at lower fluences. The observed yield of  $\text{CBr}_2\text{F}_2$  was as large as 0.75 at the highest focal fluences studied. Shown in the middle part are the yields of  $\text{CBrF}_3$  and  $\text{CHBrClF}$ . Above  $2.3 \text{ J/cm}^2$  the yields of these products were found to saturate or slightly decrease with an increase in focal fluence; this result cannot be expected from the trend observed at lower fluences.

The most notable feature in product distribution in Figure 5 (the upper part) is that new scavenged products,  $\text{CBrF}_2$ - $\text{CBrClF}$  and  $\text{CBr}_2\text{ClF}$ , appeared at fluences higher than that in Figure 4. These bromides can be the brominated products of  $\text{CF}_2=\text{CClF}$  olefins and  $\text{CClF}$  carbenes, respectively.



The formation of  $\text{CF}_2=\text{CClF}$  olefins strongly suggests that HF molecular elimination in Eq. (3) (probably four-centered elimination on energetical ground<sup>10</sup>) occurred at higher fluences.

#### Sensitization with $\text{SiF}_4$

Since no studies have been reported on the thermal reaction of  $\text{CF}_3\text{CHClF}$  with  $\text{Br}_2$  in the gas phase,  $\text{SiF}_4$ -sensitized shock-heating of a  $\text{CF}_3\text{CHClF}/\text{Br}_2$  mixture was studied to evaluate the thermal effect in the IRMPD of  $\text{CF}_3\text{CHClF}$  in the presence of  $\text{Br}_2$ . The experimental conditions and results are summarized in Table I. The maximum temperature attained in the reaction system ( $T_{\text{max}}$ ) was calculated by assuming that the absorbed energy ( $E_{\text{abs}}$ ) was adiabatically thermalized within the irradiation volume,

$$E_{\text{abs}} = \int_{298}^{T_{\text{max}}} (\sum_i n_i C_{v,i}) dT \quad (15)$$

where  $n_i$  and  $C_{v,i}$  are the molar concentrations and the spe-

cific heats for CF<sub>3</sub>CHClF (i=1), Br<sub>2</sub> (i=2), and SiF<sub>4</sub> (i=3); the values calculated for T<sub>max</sub> ranged from 660-1220 K.

TABLE I SiF<sub>4</sub>-sensitized heating of CF<sub>3</sub>CHClF/Br<sub>2</sub>

CF <sub>3</sub> CHClF (Torr)	Br <sub>2</sub> (Torr)	SiF <sub>4</sub> (Torr)	Incident <sup>a)</sup> fluence (J/cm <sup>2</sup> )	E <sub>abs</sub> (mJ)	< n > <sup>b)</sup>	T <sub>max</sub> (K)
0.5	10	5	0.40	38	4.1	660
0.5	10	5	1.44	78	9.1	1050
0.5	10	10	1.46	150	8.7	1220

a) 9P(34) 1033.5 cm<sup>-1</sup> (unfocused beam).

b) Average number of photons absorbed per molecule of SiF<sub>4</sub>.

Under these conditions no decomposition of CF<sub>3</sub>CHClF was observed within the detection limits after 1000-pulse irradiation. Thus the upper limit estimated for the dissociation probability of CF<sub>3</sub>CHClF in the sensitization experiments is as low as  $1 \times 10^{-4}$ . This value is so small that it can be concluded that the purely thermal reaction of CF<sub>3</sub>CHClF with Br<sub>2</sub> was almost negligible in the sensitization experiments.

#### Photolysis Products of Neat CF<sub>3</sub>CHClF

When CF<sub>3</sub>CHClF (100 mTorr) was irradiated in the absence of Br<sub>2</sub>, a number of irradiation products were detected by TCD. The products observed were C<sub>2</sub>F<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, CHClF<sub>2</sub>, CF<sub>2</sub>=CClF, CF<sub>3</sub>CF=CClF, CF<sub>2</sub>=CHF and a series of products C<sub>n</sub>HF<sub>2n+1</sub>, C<sub>n</sub>ClF<sub>2n+1</sub>, C<sub>n</sub>Cl<sub>2</sub>F<sub>2n</sub>, and C<sub>n</sub>F<sub>2n</sub>. Figure 6 shows the relative yields of some of the products observed in the mildly focused irradiation. The dissociation scheme was extremely difficult to construct from these photolysis products. The observed product distribution, however, suggests that the dissociation

of  $\text{CF}_3\text{CHClF}$  proceeded via plural primary pathways expressed by Eq. (1)-(4), followed by the secondary photolysis of primarily produced intermediates, which will be discussed later, and the complicate post-pulse radical reactions including Cl atoms.

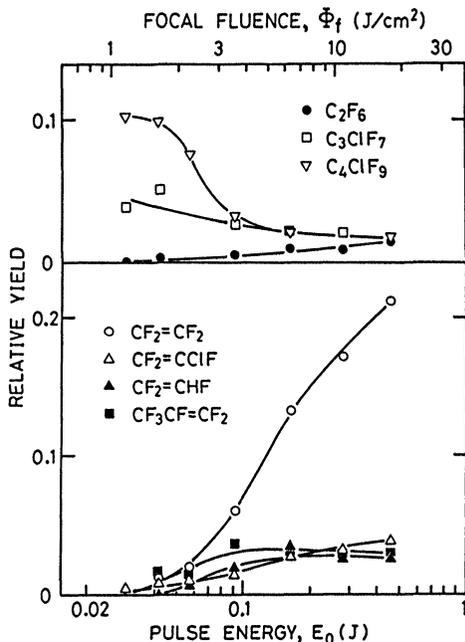


FIGURE 6. Relative yields of major products observed in irradiation of neat  $\text{CF}_3\text{CHClF}$  (100 mTorr). Relative yield was defined as in Figure 4. Irradiation conditions are the same as in Figure 5.

## DISCUSSION

### Thermal Effect

Collisions between vibrationally excited molecules and non-excited cold molecules have led almost exclusively to de-excitation of the hot molecules in IRMPD, i.e., the attempts

to induce bimolecular reactions by pulsed infrared lasers have not been very successful.<sup>1,13</sup> Such reactions have been observed only when one reactant is a gaseous atom as in the reaction  $\text{SF}_6^* + \text{Na}$ .<sup>14</sup> Although Popok et al.<sup>15</sup> irradiated  $\text{CHClF}_2$  in the presence of  $\text{Br}_2$  and observed the bromination of the reactant yielding  $\text{CBrClF}_2$ , this reaction was interpreted in terms of a radical chain reaction initiated by the reaction of Br atoms with hot  $\text{CHClF}_2$  molecules, not a direct bimolecular reaction between  $\text{CHClF}_2^*$  and  $\text{Br}_2$ .

Before discussing the possibility of thermal effects in the present IRMPD study, two notable studies should be mentioned briefly: Popok et al.<sup>15</sup> and Grunwald et al.<sup>16</sup> investigated the intermolecular energy transfer from shock-heated  $\text{SiF}_4$  to  $\text{Br}_2$ . On irradiating 12 Torr of  $\text{SiF}_4$  in the presence of 40 Torr of  $\text{Br}_2$  with a TEA  $\text{CO}_2$  laser, they obtained the thermal equilibrium temperature ( $T_{\text{max}}$ ) in the same manner as in Eq. (15) to be  $1370 \pm 70$  K. At the same time they measured the vibrational temperature of  $\text{Br}_2$  from the real-time  $\text{Br}_2$  optical absorbance to be  $1260 \pm 60$  K, which agrees with the above  $T_{\text{max}}$  within statistical errors. Their results indicate that the V/T/R thermal equilibrium process is efficient in the  $\text{SiF}_4/\text{Br}_2$  system under the relatively high pressure conditions, and the  $T_{\text{max}}$  can be calculated from Eq. (15) with sufficient accuracy.

In our  $\text{SiF}_4$ -sensitized heating of a  $\text{CF}_3\text{CHClF}/\text{Br}_2$  mixture performed under the similar experimental conditions (Table I), therefore, the calculated  $T_{\text{max}}$  values (660-1220 K) must be reliable on the basis of their results. No observation of  $\text{CF}_3\text{CHClF}$  decomposition indicates that a purely thermal reaction between  $\text{CF}_3\text{CHClF}$  and  $\text{Br}_2$  should be negligible in the sensitization experiments in the temperature range between 660-1220 K. Since the maximum temperature attainable in the

present IRMPD of  $\text{CF}_3\text{CHClF}$  in the presence of  $\text{Br}_2$  was at most 700 K, the thermal reaction of  $\text{CF}_3\text{CHClF}$  with  $\text{Br}_2$  can also be negligible (the  $T_{\text{max}}$  in IRMPD was estimated in the same manner by assuming that considerably large  $E_{\text{abs}}$  such as 150 kcal/mol or more is thermalized within the focal volume). No observation of the bromination product,  $\text{CF}_3\text{CBrClF}$ , also supports the above conclusion. The absence of the thermal reaction with  $\text{Br}_2$  is characteristic of the IRMPD of  $\text{CF}_3\text{CHF}_2$ ,<sup>3</sup>  $\text{CF}_3\text{CF}_2\text{-CHF}_2$ ,<sup>4</sup> and  $\text{CF}_3\text{CHClF}$ ; this result is probably due to the strong polarity in C-H bonds of these highly fluorinated ethanes or propanes.<sup>17</sup>

#### Primary Dissociation Processes

In the IRMPD of  $\text{CF}_3\text{CHF}_2$ <sup>3</sup> and  $\text{CF}_3\text{CF}_2\text{CHF}_2$ ,<sup>4</sup> the primary pathways were the HF molecular elimination and C-C bond rupture(s). The  $\text{Br}_2$ -scavenging technique revealed that the dissociation proceeded mainly via the high-activation-energy C-C rupture channel(s), which was also supported by the RRKM calculations for two dissociation channels. The IRMPD of  $\text{CF}_3\text{CHClF}$ , on the other hand, proceeded mainly via the three-centered HCl elimination and C-Cl bond rupture (Figures 4 and 5). The C-C bond rupture and HF molecular elimination were rather minor processes as far as the present fluence region is concerned. This may be reasonable since the unimolecular dissociation rate constants for HCl elimination and C-Cl bond rupture channels are expected to be too high at these excitation levels for further optical pumping to occur in favor of other high dissociation channels.

In the light of extensive studies on the unimolecular reactions of chlorinated and fluorinated ethanes,<sup>10,18-19</sup> it is somewhat surprising that in the IRMPD of  $\text{CF}_3\text{CHClF}$  the contribution of HF elimination was found rather small compared

with those of HCl elimination and C-Cl rupture. The Arrhenius parameters for the HF elimination and HCl elimination differ not so significantly in most monohalogenated compounds, e.g., 13-14 for log A and about 60 kcal/mol for  $E_a$ . The bond dissociation energies for C-Cl rupture usually ranges from 79-84 kcal/mol,<sup>19</sup> which are much larger than those for HF elimination.

Recent studies on the decomposition of highly fluorinated carbons, however, have shown that the activation energy for HF molecular elimination tends to be high by substituting H atoms with F atoms, e.g., 59.9 kcal/mol for  $\text{C}_2\text{H}_2\text{F}$ , 66.6 kcal/mol for  $\text{CH}_3\text{CHF}_2$ , and 71.1 kcal/mol for  $\text{CH}_3\text{CF}_3$ .<sup>18</sup> Such high  $E_a$  values are also found in HF elimination of  $\text{CHF}_2\text{CHF}_2$  (69.4 kcal/mol)<sup>20</sup> and  $\text{CF}_3\text{CHF}_2$  (71.6 kcal/mol).<sup>21</sup> Therefore, the competitive reaction for such highly fluorinated chlorocarbons can be expected to be rather complicated depending upon molecular properties and excitation conditions: In the molecular beam study of the IRMPD of  $\text{CH}_3\text{CClF}_2$ ,<sup>22</sup> Sudbø et al. observed only HCl molecular elimination in the fluence region between 5 and 10  $\text{J}/\text{cm}^2$ . West et al.<sup>23</sup> who irradiated the same molecule at higher fluences (60-400  $\text{J}/\text{cm}^2$ ) observed infrared emissions from HCl\* and HF\*, although they did not confirm whether the HF emission arose from the primary process or secondary photolysis. In the shock-tube pyrolysis of  $\text{CF}_3\text{CH}_2\text{Cl}$ ,<sup>24</sup> the first example of the three-centered HCl elimination was demonstrated together with a competing HF elimination channel between 1120 and 1300 K. Whereas HF elimination was observed in the pyrolysis of  $\text{CF}_3\text{CH}_2\text{Cl}$ , the shock-tube pyrolysis of a similar molecule,  $\text{CF}_3\text{CHCl}_2$ ,<sup>25</sup> was found to proceed via different pathways, i.e., three-centered HCl elimination and C-Cl rupture. The HF elimination was rather a negligible process, whereas C-C bond rupture occurred at temperatures

above 1260 K. The IRMPD of deuterated  $\text{CF}_3\text{CHCl}_2$  ( $\text{CF}_3\text{CDCl}_2$ ) was studied for LIS of deuterium by Marling *et al.*,<sup>26-27</sup> who reported that the major primary process was the C-Cl bond rupture at fluences above  $10 \text{ J/cm}^2$ .

The IRMPD of  $\text{CF}_3\text{CHClF}$  was found to proceed in exactly the same manner as in the pyrolysis of  $\text{CF}_3\text{CHCl}_2$ . Figure 7 shows the atomic mass balance for F, H, and Cl observed in the scavenged products. The carbon mass balance was almost 100 % as stated previously.

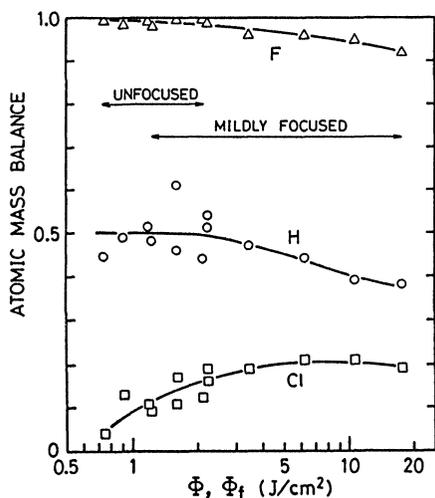


FIGURE 7. Atomic mass balance for F ( $\Delta$ ), H ( $\circ$ ), and Cl ( $\square$ ) observed in the scavenged products (Figures 4 and 5) as a function of fluence ( $\Phi$ ) or focal fluence ( $\Phi_f$ ).

The atomic balance for Cl was found to be nearly null at the lowest fluence, indicating that the primary processes losing Cl atoms (HCl elimination and C-Cl bond rupture) were dominant processes at such a low fluence region. The presence of several chlorocarbon products in the IRMPD of neat  $\text{CF}_3\text{CHClF}$

(Figure 6) also supports the C-Cl bond rupture at low fluences. With an increase in fluence, the Cl atomic balance was found to increase gradually. This behavior can be explained in terms of HCl elimination and C-Cl bond rupture predominated by other primary processes (C-C bond rupture and HF elimination) at higher levels of excitation. We will discuss the atomic balance for F and H in the following section, taking the secondary photolysis processes into account.

### Secondary Photolysis

If the Arrhenius parameters for CF<sub>3</sub>CHClF dissociation are assumed to be similar to those for CF<sub>3</sub>CHCl<sub>2</sub> (log A = 13.4 and E<sub>a</sub> = 63.1 kcal/mol for HCl elimination, log A = 16 and E<sub>a</sub> = 78 kcal/mol for C-Cl rupture),<sup>25</sup> the branching ratio (C-Cl rupture / HCl elimination) should increase dramatically with the degree of excitation as has been predicted in the RRKM calculations for CF<sub>3</sub>CF<sub>2</sub>CHF<sub>2</sub><sup>4</sup> with a similar set of Arrhenius parameters. The observed branching ratio, however, disagrees with above expectation (Figure 5). The C-Cl/HCl value decreased from 0.8 to 0.5 with an increase in focal fluence. Moreover, unexpected scavenged products (CBr<sub>2</sub>F<sub>2</sub>, CBr<sub>2</sub>ClF, and CHBrF<sub>2</sub>) appeared, the yields of which increased with an increase in focal fluence. This product distribution may be accounted for by the secondary photolysis of the intermediates primarily produced during the laser pulse. Such secondary photolysis has proved to play a significant role in the IRMPD of CF<sub>3</sub>CHF<sub>2</sub><sup>3</sup> and CF<sub>3</sub>CF<sub>2</sub>CHF<sub>2</sub>.<sup>4</sup>

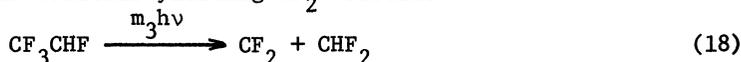
The origin of CBr<sub>2</sub>F<sub>2</sub>, the scavenged product of CF<sub>2</sub> carbenes, can be attributed partly to the secondary photolyses of CF<sub>3</sub> radicals from C-C rupture and CF<sub>2</sub>=CClF olefins from HF elimination.





The secondary photolysis of  $\text{CF}_3$  radicals has been reported in the literature.<sup>3-4,28-29</sup> The IRMPD of  $\text{CF}_2=\text{CClF}$  was studied by Stephenson *et al.*<sup>30</sup> using an LIF technique to monitor  $\text{CF}_2$  and  $\text{CClF}$  carbenes. Also in our static cell experiments we confirmed that  $\text{CF}_2=\text{CClF}$  efficiently absorbed IR photons at  $9\text{R}(20) 1078.6 \text{ cm}^{-1}$  to yield recombination products of  $\text{CF}_2$  and  $\text{CClF}$  carbenes ( $\text{CF}_2=\text{CF}_2$ ,  $\text{CClF}=\text{CClF}$ ,  $\text{C}_3\text{ClF}_5$ , and  $\text{C}_3\text{Cl}_2\text{F}_4$ ); this result also supports the secondary dissociation mechanism in Eq. (17). According to this mechanism, the increasing yield of  $\text{CBr}_2\text{ClF}$  with an increase in  $\phi_f$  (the upper part in Figure 5) results in the increasing contribution of HF elimination process from  $\text{CF}_3\text{CHClF}$  (Eq. (3)). The slightly decreasing mass balance for H and F atoms at higher fluences (Figure 7) may well be explained based on the above processes.

The yield of  $\text{CBr}_2\text{F}_2$  at higher fluences, however, seems to be too large to be explained adequately only by Eq. (16) and (17). One possibility is the secondary photolysis of  $\text{CF}_3\text{CHF}$  radicals yielding  $\text{CF}_2$  carbenes.



There is no evidence for C-C rupture ( $\text{CF}_3\text{CHF} \longrightarrow \text{CF}_3 + \text{CHF}$ ) or C-F rupture ( $\text{CF}_3\text{CHF} \longrightarrow \text{CF}_2=\text{CHF} + \text{F}$ ) in  $\text{CF}_3\text{CHF}$  dissociation, because neither the scavenged product of  $\text{CHF}$  nor  $\text{CF}_2=\text{CHF}$  ( $\text{CHBr}_2\text{F}$  nor  $\text{CBrF}_2\text{CHBrF}$ ) was observed even in trace amounts. The absence of  $\text{C}_2\text{Br}_3\text{F}_3$  also excludes the HF elimination from  $\text{CF}_3\text{CHF}$  radicals. Although no studies have been reported on the decomposition of  $\text{CF}_3\text{CHF}$  radicals, our careful GC/MS analysis revealed that the scavenged product  $\text{CF}_3\text{CHBrF}$  contained a small amount of its isomer  $\text{CBrF}_2\text{CHF}_2$  ( $\approx 5\%$ ), which might be a scavenged product of  $\text{CF}_2\text{CHF}_2$  intermediate

in the decomposition of CF<sub>3</sub>CHF radicals in Eq. (18). This secondary-photolysis mechanism seems somewhat special, but can well account for the rapid decrease in CF<sub>3</sub>CHBrF yield, the rapid increase in CBr<sub>2</sub>F<sub>2</sub> yield, and the formation of CHBrF<sub>2</sub> at high fluences shown in Figure 5.

Another mechanism which can be responsible for the formation of CBr<sub>2</sub>F<sub>2</sub> is the secondary photolysis of CF<sub>3</sub>CF carbenes produced by Eq. (1).



The CF<sub>3</sub>CF carbenes are reported to be exceptionally stable among other asymmetric carbenes;<sup>31</sup> no isomerization to CF<sub>2</sub>=CF<sub>2</sub> was observed at 200°C. In the IRMPD, however, nascent CF<sub>3</sub>CF could further absorb photons to be excited to much higher vibrational levels, yielding CF<sub>2</sub> carbenes as in Eq. (19).

As discussed above, there are many possible routes producing CF<sub>2</sub> carbenes. No quantitative discussion is possible on the basis of the product distribution solely. The secondary photolysis of CHClF radicals, the matrix-isolation spectrum of which<sup>32</sup> was reported to have IR peaks at 1151 and 1283 cm<sup>-1</sup>, was not revealed in the present study either. However, the formation of a marked amount of CF<sub>2</sub> via the secondary photolysis seems to be characteristic of the IRMPD of such highly fluorinated carbons as CF<sub>3</sub>CHF<sub>2</sub>,<sup>3</sup> CF<sub>3</sub>CF<sub>2</sub>CHF<sub>2</sub>,<sup>4</sup> and CF<sub>3</sub>CHClF. A rapid increase in the yield of C<sub>2</sub>F<sub>4</sub> (the recombination product of two CF<sub>2</sub> carbenes) shown in Figure 6 also strongly suggests the formation of CF<sub>2</sub> carbenes at high fluences.

## CONCLUSION

Primary dissociation mechanisms in the IRMPD of CF<sub>3</sub>CHClF were

revealed by Br<sub>2</sub>-scavenging technique. The major processes were the three-centered HCl elimination and the C-Cl bond rupture. Minor contributions of C-C bond rupture and HF elimination were also observed at high laser fluences. The SiF<sub>4</sub>-sensitized heating experiments of a CF<sub>3</sub>CHClF/Br<sub>2</sub> mixture confirmed that the IRMPD of CF<sub>3</sub>CHClF proceeded unimolecularly.

The secondary photolysis of the primarily produced species was found to occur fairly efficiently depending upon the laser fluence, as revealed in our previous studies of the IRMPD of CF<sub>3</sub>CHF<sub>2</sub> and CF<sub>3</sub>CF<sub>2</sub>CHF<sub>2</sub>. The secondary photolysis has now become recognized as an important factor controlling final products in IRMPD; its application to the laser radical synthesis has already appeared in the literature.<sup>2,7,33</sup>

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