# Infrared Multiphoton Dissociation of CHCl₂F: Reaction Mechanisms and Product Ratio Dependence on Pressure and Laser Pulse Energy

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Infrared multiphoton dissociation of $CHCl_2F$ was studied using $CO_2$ laser excitation. Three products, $C_2Cl_2F_2$, $C_2ClF_3$, and $C_2HClF_2$, were identified by the analysis of the gas mixture from the photoreaction of $CHCl_2F$. The dependence of the reaction probability on added Ar gas pressure and excitation laser pulse energy was investigated. At low pressure (< 10 torr), the reaction probability increased as Ar pressure increased due to the rotational hole-filling effect, while it diminished with the increase of Ar pressure at high pressure (> 20 torr) due to the collisional deactivation. The ratio of two products ($C_2ClF_3/C_2Cl_2F_2$) decreased at low pressure (< 10 torr) and increased at high pressure (> 20 torr) with the increase of Ar pressure. The log-log plot of the reaction probability *vs.* laser pulse energy ($\phi$) was found to have a linear relationship, and its slope decreased as the added Ar pressure was increased. The reaction mechanisms for product formation have been suggested and validated by experimental evidences and considering the energetics. Fluorine-chlorine exchange reaction in the intermediate complex has been suggested to explain the formation of $C_2ClF_3$.

key words : IRMPD, $CHCl_2F$, $C_2Cl_2F_2$, $C_2ClF_3$, $C_2HClF_2$

## INTRODUCTION

Infrared multiphoton absorption (IRMPA) and subsequent decomposition (IRMPD) have been studied extensively [1-6]. One of the purposes in previous studies was mainly on the possibility of mode selective activation and dissociation. It was expected that sufficient energy could be deposited into a specific molecular vibration mode to cause reaction exclusively in that site. However, it has been observed that the energy absorbed by a molecule is quickly randomized over all internal modes, so that activation of a specific mode over dissociation level cannot be accomplished easily [2].

According to the general IRMPD theory, the vibrational manifold can be divided into two groups [2]; the discrete levels at low energy region and the quasi-continuum or true continuum levels at high energy region. In IRMPD experiments, activation process occurs from the discrete levels to the continuum region. And this excitation step is crucial especially for small molecules in which the discrete levels are spread broadly. In small molecules, the fraction of molecules that can directly absorb the laser photons is very small. And there is no more absorption of photons by molecules after the fraction of molecules are pumped to the

excited states (rotational hole burning). In the presence of Ar gases, however, the burned states can be replenished by intermolecular collisions and further absorption occurs (rotational hole-filling) [7-9].

In a thermal reaction system, the excitation of molecules occurs via molecular collisions and the energies of molecules are partitioned into translational modes. Thus exclusive excitation of vibrational states cannot be obtained. On the other hand, IRMPD provides energized molecules excited only in vibrational and rotational states. In experiments using an intense IR laser, reactions arising in high vibrational energy states can be observed and the collisional deactivation dynamics of highly excited molecules can be studied.

In this paper we present the result of the IRMPD of $CHCl_2F$. Primarily, the reaction channels were determined by the product analysis. The IRMPD of $CHCl_2F$ was found to give three products: $C_2Cl_2F_2$, $C_2ClF_3$, and $C_2HClF_2$. Then the dependence of the reaction probability on the added Ar gas pressure and the laser pulse energy was investigated. The variation of the product ratio with the added Ar gas pressure and the laser pulse energy was also investigated. Finally, the reaction mechanisms for product formation have been suggested and validated by experimental evidences and considering the energetics.

## EXPERIMENTAL

The schematic diagram of the experimental setup is shown in Fig. 1. A TEA $CO_2$ laser (Tachisto 215G) was used as the radiation source. The laser pulse consists of 40 ns gain switched spike and 500 ns low intensity tail. The wavelength of the laser light was measured by using a spectrum analyzer (Scientech Inc.). The irradiation line was R12 (1073.3cm$^{-1}$) which is resonant with C-F stretching mode of $CHCl_2F$ [10]. To provide a more homogeneous beam, the beam size was reduced with an iris diaphragm. The laser pulse energy was varied by attenuation of the incident beam with polystyrene films. The laser pulse energy was measured using a pyroelectric detector (Scientech 36-2001). A pulse to pulse stability in energy was found to be $ca. \pm 3$ %.

The reaction cell (10 cm long and 2.0 cm inner diameter) was made of a cylindrical Pyrex tube with NaCl windows attached at both ends. The NaCl windows were sealed to the tube with "Torr Seal" vacuum epoxy resin (Varian Co.). In the absorption experiment, a parallel beam was passed through a long gas cell (1 m in pathlength) without being focused. Measurements were made with the sample pressure of 5 torr.

In the dissociation experiments, the beam was focused into the center of the reaction cell using a ZnSe lens (f = 15 cm). The reaction products were accumulated for 1000 laser shots to obtain a detectable quantity for our analysis condition. The components in the laser irradiated gas mixture were analyzed by using a gas chromatograph (GC, Yanaco G-80) connected to a FID detector. A Hall M-18-OL column of 2 × 2.4 m length was used at 58°C. The output signal of GC was stored and integrated in a computer.

The sample pressure was measured in an MKS Baratron 0 - 1 torr electric pressure transducer. The pressure of the added Ar gas was monitored using an MKS Baratron 0 - 100 torr pressure transducer. The molecular beam mass spectrometer (UTI, model 100C) detection system was used for the mass analysis of photoproducts. $CHCl_2F$, purchased from Aldrich Chemical Co. (≥98%) was used without further purification.
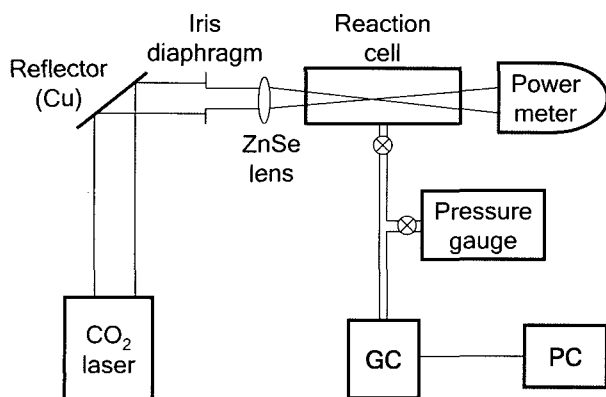
Ar (Research Grade) was obtained from Matheson Co.. $C_2Cl_2F_2$ (PCR Research Chemicals) and $C_2ClF_3$ (Aldrich Chemical Co.) were used for the product identification.

## RESULTS

*Photoproduct identification*

We obtained three major GC peaks after the irradiation of $CHCl_2F$ with a focused IR laser. These products were identified by comparing the GC retention times of the photoproducts with those of the high purity authentic samples. Mass spectroscopic analysis was also used for the identification of photoproducts.

1. Product 1 (CFCl=CFCl)

It is expected that :CFCl radical is produced through the three-center elimination reaction of HCl in the dissociation of $CHCl_2F$. Halocarbens readily combine each other resulting in the production of dihaloethene (CFCl=CFCl) as reported previously in the IRMPD of $CF_2HCl$ [7]. It was identified by the mass spectrometric analysis on the photoproducts as the mass peak at m/e = 132 with corresponding natural Cl isotope abundances. By comparing the GC retention time of a pure CFCl=CFCl and those of products, we found that the third peak coincided with the $C_2Cl_2F_2$ peak.

2. Product 2 ($CF_2$=CFCl)

$C_2ClF_3$ was identified as the mass peak at m/e = 116. Further identification was done by comparing the GC retention time with pure authentic sample.

3. Product 3 ($C_2HClF_2$)

This is a minor product which was produced only at low Ar gas pressure and excited by low laser pulse energy. We assigned the mass peak at m/e = 98 as that of $C_2HClF_2$.

*Absorption cross-section measurement*

The absorption cross-section of a small molecule for laser pulse is known to be dependent upon the total pressure of the system at low pressures [11, 12]. $CHCl_2F$ of 5 torr was used for the absorption measurement and it was assumed that the pressure is high enough to neglect the rotational hole-burning and hole-filling effects [7-9]. As the C-F stretching band of $CHCl_2F$ is observed around 1080 cm$^{-1}$ [10], the absorption cross-section for laser pulse near 1080 cm$^{-1}$ was measured at the laser energy of 200 mJ. The absorption cross-section ($\sigma$) was calculated by using the Beer-Lambert's law [12] as

$$\sigma(f) = - (1/Nl) \ln T \tag{1}$$

$\phi$ : laser pulse energy
T : transmittance
N : number of molecules per unit volume
l : optical pathlength of the gas cell



**Figure 1.** Schematic diagram of the experimental setup.

The results are represented in Table 1 and Fig. 2. As shown in Fig. 2, two maxima were observed at 1085.8 $cm^{-1}$ (R32) and 1073.3 $cm^{-1}$ (R12). We used the laser line of 1073.3 $cm^{-1}$ (R12) for all experiments since the output of this line is higher and more stable than R32 line. The dependence of the absorption cross-section on the laser pulse energy at R12 line is represented in Fig. 3. The absorption cross section decreased as the laser pulse energy increased. This result agrees with general observations that an absorption cross-section decreases with the increase of the internal energy of molecules [13].

*Pressure and pulse energy dependence of reaction probability and branching ratio*

The reaction probability of $CHCl_2F$ was measured as a

**Table 1.** The measured absorption cross-section of $CHCl_2F^a$ at various $CO_2$ laser lines.

| Wavenumber $(cm^{-1})$ | Cross-section $(cm^2)$ | Line number |
|---|---|---|
| 1035.5 | $2.19 \times 10^{-20}$ | P32 |
| 1039.4 | $1.87 \times 10^{-21}$ | P28 |
| 1043.2 | $2.46 \times 10^{-20}$ | P24 |
| 1046.9 | $2.95 \times 10^{-21}$ | P20 |
| 1050.4 | $3.71 \times 10^{-21}$ | P16 |
| 1053.9 | $2.42 \times 10^{-20}$ | P12 |
| 1057.3 | $6.82 \times 10^{-20}$ | P8 |
| 1070.5 | $1.23 \times 10^{-19}$ | R8 |
| 1073.3 | $1.92 \times 10^{-19}$ | R12 |
| 1076.0 | $1.55 \times 10^{-19}$ | R16 |
| 1078.6 | $1.53 \times 10^{-19}$ | R20 |
| 1081.1 | $1.63 \times 10^{-19}$ | R24 |
| 1083.5 | $2.00 \times 10^{-19}$ | R28 |
| 1085.8 | $2.13 \times 10^{-19}$ | R32 |
| 1087.9 | $1.68 \times 10^{-19}$ | R36 |

a. The pressure of reactant was 5.0 torr.
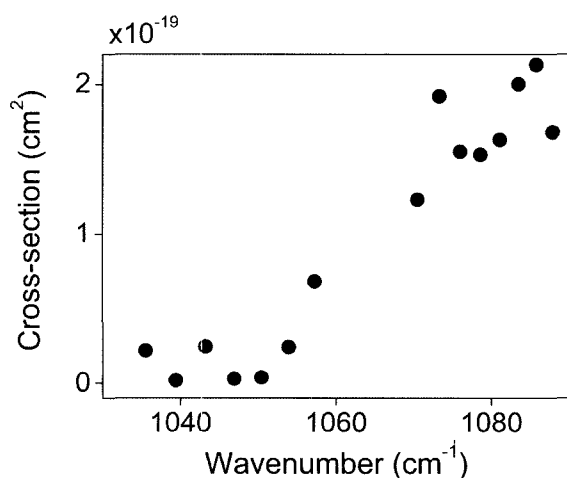b. The laser pulse energy was 200 mJ.



**Figure 2.** Measured absorption cross-section of $CHCl_2F$ at various laser lines.

function of laser pulse energy and the pressure of added Ar gas. The results are represented in Figs. 4 and 5. The reaction probability per pulse, $\alpha$, is given by the following equation.

$$\alpha = -(1/n) \ln ([A]/[A]_o) \qquad (2)$$

n : the number of pulses
$[A]_o$ : concentration of the sample before photodissociation
$[A]$ : concentration of the sample after photodissociation

The dependence of the reaction probability on laser pulse energy was measured at various Ar pressures. As shown in Fig. 4, the log-log plot of the reaction probability vs. laser pulse energy ($\phi$) was found to have a linear relationship, i.e., $\ln \alpha \propto \beta \ln \phi$. $\beta$ was found to have lower value at high pressures than at low pressures.

As shown in Fig. 5, the rotational hole-filling effect which frequently occurs in the IRMPD of small molecules was observed [7-9, 11]. At low pressure ($< 10$ torr), the reaction
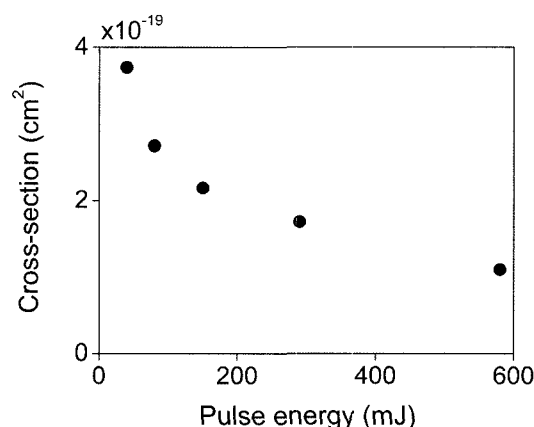


**Figure 3.** Measured absorption cross-section of $CHCl_2F$ vs. laser pulse energy. Absorption of R12 line (1073.3 $cm^{-1}$) was measured.
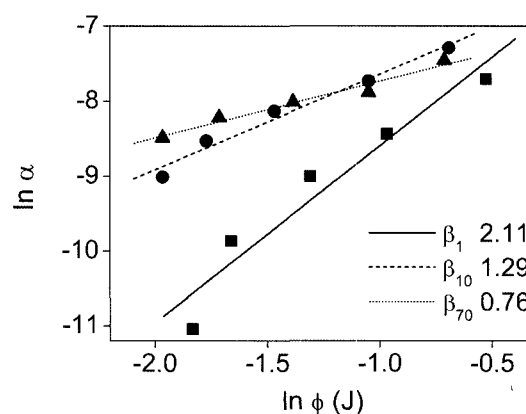


**Figure 4.** Dependence of reaction probability of $CHCl_2F$ on the laser pulse energy (f) at different added Ar pressures. (■ : 1 torr,●: 10 torr, : ▲70 torr) ($\beta$ is the slope of the plot for $\ln \alpha$ vs. $\ln \phi$.)
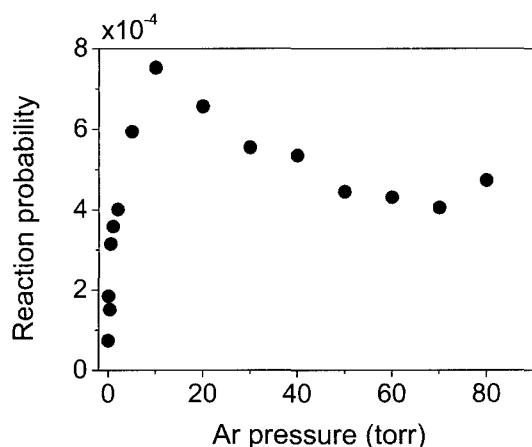
**Figure 5.** Dependence of reaction probability of $CHCl_2F$ on the added Ar pressure. (Laser pulse energy was 500 mJ.)



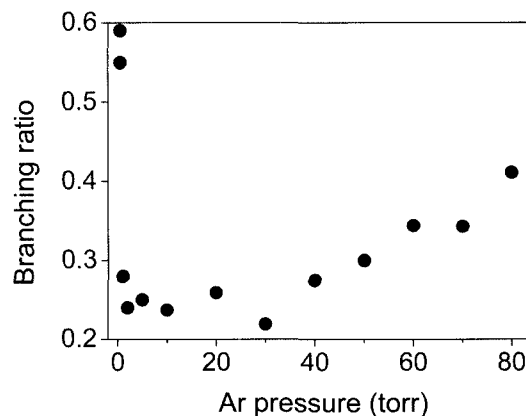**Figure 6.** Dependence of the relative product ratio ($C_2Cl_2F_2/C_2ClF_3$) on the added Ar pressure. (Laser pulse energy was 500 mJ.)

probability increased as the pressure of Ar gas increased. At high pressure (> 20 torr) the reaction probability diminished with the increase of Ar gas pressure because of the collisional deactivation. The dependence of the product formation on Ar gas pressure and the laser pulse energy is represented in Tables 2 and 3. $C_2Cl_2F_2$ was always the major product under our experimental conditions. At constant pulse energy, the $C_2Cl_2F_2$ product increased with Ar pressure up to 20 torr, but it decreased above 40 torr. In contrast to $C_2Cl_2F_2$, the amount of $C_2ClF_3$ produced increased with the increase of Ar gas pressure. Thus, the ratio of two products ($C_2ClF_3/C_2Cl_2F_2$) decreased with the increase of pressure at low pressure region (<10 torr) and increased at high pressure region (>10 torr) (Table 2, Fig. 6).

At constant pressure, the total amount of two products produced decreased as the laser pulse energy was reduced.

However, the product ratio showed no dependence on the laser pulse energy (Table 3). At the laser energy of 500 mJ/ pulse, $C_2HClF_2$ was produced only below 5 torr of Ar gas pressure. The amount of $C_2HClF_2$ produced increased as the pressure decreased. It became the major product when no Ar gas was added. At constant Ar gas pressure the ratios of $[C_2HClF_2]/[C_2Cl_2F_2]$ and $[C_2HClF_2]/[C_2ClF_3]$ increased as the laser energy decreased.

## DISCUSSION

*The reaction mechanisms of product formation.*

As mentioned previously the major products are $C_2Cl_2F_2$, $C_2ClF_3$, and $C_2HClF_2$. Possible mechanisms for each product formation are suggested as follows.

**Table 2.** The formation probability of $C_2ClF_3$ and $C_2Cl_2F_2$ at various Ar pressures.

| Pressure of added Ar gas (torr) | $C_2ClF_3$ ($\times10^{-5}$) | $C_2Cl_2F_2$ ($\times10^{-4}$) | Branching ratio $[C_2ClF_3]/[C_2Cl_2F_2]$ |
|---|---|---|---|
| 0.4 | 3.06 | 0.52 | 0.59 |
| 0.5 | 2.52 | 0.46 | 0.55 |
| 1.0 | 1.81 | 0.65 | 0.28 |
| 2.0 | 1.42 | 0.59 | 0.24 |
| 5.0 | 2.50 | 1.01 | 0.25 |
| 10.0 | 3.48 | 1.47 | 0.237 |
| 20.0 | 3.91 | 1.51 | 0.259 |
| 30.0 | 3.63 | 1.66 | 0.219 |
| 40.0 | 4.49 | 1.63 | 0.275 |
| 50.0 | 3.66 | 1.22 | 0.300 |
| 60.0 | 4.03 | 1.17 | 0.344 |
| 70.0 | 4.11 | 1.20 | 0.343 |
| 80.0 | 5.02 | 1.22 | 0.411 |

a. The pressure of reactant was 0.04 torr.
b. The laser pulse energy was 500 mJ.

**Table 3.** The dependence of $C_2ClF_3$ and $C_2Cl_2F_2$ formation probability on the laser energy with added Ar gas

| Pressure of Ar gas (torr) | Energy per pulse (mJ) | $C_2ClF_3$ ($\times10^{-5}$) | $C_2Cl_2F_2$ ($\times10^{-5}$) | Branching[a] ration |
|---|---|---|---|---|
|  | 590 | 1.35 | 2.31 | 0.584 |
|  | 380 | 1.10 | 2.29 | 0.480 |
| 1.0 | 270 | 0.73 | 2.18 | 0.33 |
|  | 190 | 0.66 | 1.28 | 0.52 |
|  | 160 | 0.96 | 1.50 | 0.64 |
|  | 500 | 1.93 | 7.98 | 0.242 |
|  | 350 | 1.02 | 5.22 | 0.195 |
| 10.0 | 230 | 0.85 | 4.44 | 0.19 |
|  | 170 | 0.76 | 3.80 | 0.20 |
|  | 140 | 0.41 | 2.19 | 0.19 |
|  | 490 | 2.23 | 6.00 | 0.372 |
|  | 350 | 1.27 | 3.99 | 0.318 |
| 70.0 | 250 | 1.76 | 4.00 | 0.440 |
|  | 180 | 1.29 | 3.34 | 0.386 |
|  | 140 | 1.38 | 2.93 | 0.471 |

a. The ratio of $[C_2ClF_3]/[C_2Cl_2F_2]$.
b. The pressure of reactant was 0.04 torr.

## 1. $C_2Cl_2F_2$

It is well known that IRMPD of halomethanes such as $CHCl_2F$ and $CHClF_2$ proceeds by three-center elimination reaction to generate halocarbenes (:CFCl or :CF₂) [5,7]. :CFCl recombines to produce $C_2Cl_2F_2$. The mechanism is suggested as Eqs. (3) and (4) in Scheme 1. Reaction (3), the removal of HCl through three-center elimination, is expected to be the lowest activation energy channel of all the possible dissociation channels of $CHCl_2F$ since the simple bond fission reactions of any single bond are expected to have much higher activation energies [5,14].

## 2. $C_2ClF_3$

This product was identified by the mass peak at m/e = 116 and the comparison of GC retention times with a pure authentic sample. As the reactant molecule contains only one F atom, the production mechanism of $C_2ClF_3$ could not be explained by a one step reaction. It was assumed that $C_2ClF_3$ was produced by the addition of :CFCl carbene to the primary product, $C_2Cl_2F_2$, followed by a fluorine-chlorine exchange reaction. Corresponding mechanism can be suggested as Eqs. (3)~(7) in Scheme 1. To confirm that :CFCl effectively inserts to the ethylene in reaction (5), we irradiated the mixture of $CHCl_2F$ and $C_2Cl_2F_2$. The amount of reduced $C_2Cl_2F_2$ was much larger than that when the only $C_2Cl_2F_2$ sample was irradiated at the same laser line. The result can be an evidence for the assumption that reaction (5) occurs with a sufficiently large rate constant.

To check if a monovalent radical, e.g. F atom or $CFCl_2$, is involved in the reaction process, the mixture of $CHCl_2F$ and NO, a radical scavenger, was irradiated. Since the production rate of $C_2ClF_3$ was not affected by the addition of NO, it could be confirmed that no radical species was involved in the production of $C_2ClF_3$. As a result, reaction (6), which is not expected to occur easily, is the only pathway that can be suggested. Fluorine-chlorine exchange reaction has been previously
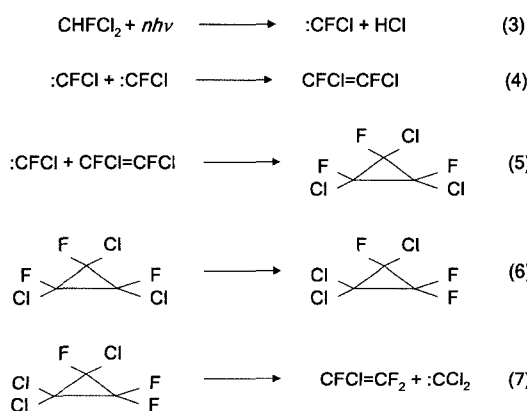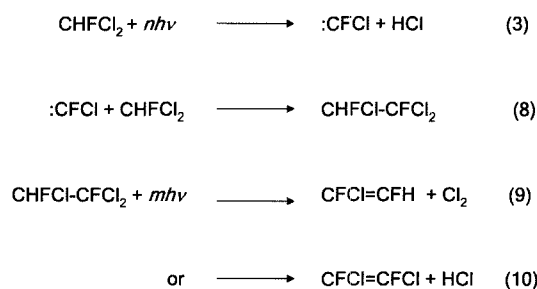
proposed in other IRMPD experiments [15]. Migration of fluorine atoms has also been suggested in the reactions of highly energized molecules [16-19].

Relative formation probability of $C_2ClF_3$ compared with $C_2Cl_2F_2$ initially decreased with addition of Ar gas up to 10 torr, however it was slightly increased with Ar gas addition above 10 torr (Table 2, Fig. 6). The reason why the branching ratio, $[C_2ClF_3]/[C_2Cl_2F_2]$, was increased with the addition of Ar gas above 10 torr might be suggested that the triangular intermediate in reaction (5) could be more stabilized as the Ar gas pressure was increased. Since the triangular reaction intermediate is expected to be very unstable, collisional deactivation of the intermediate by added Ar gas would help the fluorine-chlorine exchange reaction occur more efficiently by stabilizing the intermediate. The reason for the initial decrease of the branching ratio with Ar addition is not clear.

## 3. $C_2HClF_2$.

This product was identified by the mass peak at m/e = 98, and could be detected only at low pulse energy and low pressure conditions. According to the general IRMPD theory, molecules have different characters in view of energy content at low pressures compared with low pulse energy conditions. At low pressures, deactivation of energized molecules by collisions rarely occurs so that molecules have high internal energy. To the contrary, the low energy of laser pulse makes molecules to have little internal energy at low pulse energy conditions. As a result, a product which can be produced only at low pressures does not appear at low pulse energy conditions. Our result doesn't coincide with such trend. The fact led us to conclude that $C_2HClF_2$ production does not differ from the other products in a unimolecular dissociation step, but another secondary reaction process governs the production rate. Corresponding mechanism has been suggested as Eqs. (3), (8) and (9) in Scheme 2. Under the conditions at which $C_2HClF_2$ can be detected, the concentration of carbene is so small that reaction (8) might effectively compete with carbene-carbene recombination reaction. The anharmonicity bottleneck effect at low pressures and low internal energy of $CHCl_2F$ due to low excitation pulse energy are responsible for the dilute concentration of carbene. At such conditions, moderate



$$CHFCl_2 + nh\nu \longrightarrow :CFCl + HCl \quad (3)$$

$$:CFCl + :CFCl \longrightarrow CFCl{=}CFCl \quad (4)$$

$$:CFCl + CFCl{=}CFCl \longrightarrow \quad (5)$$

$$(6)$$

$$\longrightarrow CFCl{=}CF_2 + :CCl_2 \quad (7)$$

**Scheme 1.** Suggested reaction mechanism for $C_2Cl_2F_2$ and $C_2ClF_3$ formation.



$$CHFCl_2 + nh\nu \longrightarrow :CFCl + HCl \quad (3)$$

$$:CFCl + CHFCl_2 \longrightarrow CHFCl{-}CFCl_2 \quad (8)$$

$$CHFCl{-}CFCl_2 + mh\nu \longrightarrow CFCl{=}CFH + Cl_2 \quad (9)$$

$$or \longrightarrow CFCl{=}CFCl + HCl \quad (10)$$

**Scheme 2.** Suggested reaction mechanism for $C_2HClF_2$ formation.

internal energies in molecules which are not sufficient for decomposition might help the carbene-molecule bimolecular reaction to be enhanced. As the production rate of carbene increases, carbene-molecule reaction is expected to vanish because of low concentration of energized molecules and the requirement of higher activation energy than carbene recombination reaction. Singlet carbene which is the ground state form for dihalocarbenes can easily insert into a single bond as reaction (8) [20-22]. Although reaction (9) is expected to have higher activation energy than reaction (10), the excess energy from reaction (8) and absorption of more photons are expected to support the reaction to occur efficiently.

*The relationship between the excitation laser pulse energy and reaction probability.*

In the pulse energy dependence of IRMPD, the log-log plot of the reaction probability ($\alpha$) *vs.* the laser pulse energy ($\phi$) revealed the linear relationship, i.e., $\ln \alpha \propto \beta \ln \phi$. For IRMPD experiments with focusing geometry, it is usually known that $\beta$ value corresponds to 3/2 [23, 24]. The 3/2 power energy dependence of reaction probability could be derived from the geometrical consideration with the assumption that all molecules in a conical zone dissociate with a unit probability and ignore any reactions outside this zone [24]. If the contribution of the reaction outside the laser focus is significant, $\beta$ value becomes larger than 3/2 [24, 25]. In our experiment, $\beta$ values were observed to be in the range of 0.76 ~2.11 depending on the buffer gas pressure (Fig. 4). The $\beta$ value of 2.11 at low Ar pressure (1 torr) might be due to the contribution of the reaction outside the laser focus. Lower â values than 3/2 (0.76 and 1.29) might be attributable to the geometrical relationship between the focusing lens and reaction cell dimension. The focal length of our lens was 15 cm and the length of reaction cell was 10 cm. Since the laser focus was positioned at the center of reaction cell, both windows of the reaction cell were 5 cm apart from the focus. Thus the increase of reaction volume, in which the reaction probability corresponds to unity, was limited by the entrance and exit windows for laser pulse in our experiment since there was no reactant outside the reaction cell. This result indicated that the reaction probability reached to unity even mildly focused region at high added Ar pressure condition (10 and 70 torr). Also we could know that the length of the reaction cell should be almost same as twice of the lens focal length for readily decomposable molecules to avoid the limitation of reaction volume expansion along with the increase of laser pulse energy by the reaction cell dimension.

## CONCLUSION

As a summary, we have investigated the IRMPD of $CHCl_2F$ using $CO_2$ laser excitation. Three products, $C_2Cl_2F_2$, $C_2ClF_3$, and $C_2HClF_2$, were identified as a result of photoreaction

of $CHCl_2F$. The competition between the rotational hole-filling and collisional deactivation processes was pronounced in added Ar pressure dependence of reaction probability. The reaction probability showed initial increase with added Ar pressure up to 10 torr, and then decreased with the increase of Ar pressure afterwards. The log-log plot of the reaction probability *vs.* laser pulse energy (f) showed a linear relationship, and its slope decreased as the added Ar pressure was increased. It was interpreted as due to the geometrical relationship between the focusing lens and reaction cell. The length of the reaction cell should be almost same as twice of the lens focal length for readily decomposable molecules to avoid the limitation of reaction volume expansion along with the increase of laser pulse energy by the reaction cell dimension.

Fluorine-chlorine exchange reaction in the intermediate complex has been suggested to explain the formation of $C_2ClF_3$. Since the relative production ratios of three products were dependent on added Ar pressure and excitation laser pulse energy, the optimal condition for the efficient production of a specific compound could be determined based on the maximal branching ratios.

## ACKNOWLEDGEMENTS

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