

Effects of NH_3 on ^{13}C -Selective Infrared Multiple Photon Decomposition of CF_2HCl by a CO_2 Laser

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The effects of NH_3 on product yields and ^{13}C enrichment factors have been examined for the IRMPD of CF_2HCl using a CO_2 TEA laser. The IRMPD of neat CF_2HCl yields only C_2F_4 and HCl as final products. The addition of NH_3 resulted in the formation of CF_3H and NH_4Cl in addition to C_2F_4 , and enhanced significantly the decomposition of CF_2HCl . The enrichment factors of ^{13}C in C_2F_4 and CF_3H decreased with increasing NH_3 , but the decreases were relatively small. The mechanism of the IRMPD in the presence of NH_3 is discussed on the basis of the observed results.

It has been well-established that four-atom or larger molecules absorb numerous photons and undergo unimolecular decomposition when their resonant vibration modes are irradiated with high-fluence radiation from infrared lasers.¹⁾ The photochemical phenomenon is called infrared multiple photon decomposition (IRMPD in abbreviation). IRMPD frequently exhibits remarkable isotope effects, reflecting the relatively large isotope shifts on infrared absorption. A number of studies have been already published on isotope separation of elements from hydrogen to uranium.¹⁻³⁾ However, it is not easy to obtain practical amounts of enriched products in laser isotope separation by use of IRMPD, although selectivities are high. Recently, Kamioka et al. have succeeded in producing silicon isotopes on a practical scale using the IRMPD of Si_2F_6 .^{4,5)}

Natural carbon consists of two isotopes, i.e., 98.9% of ^{12}C and 1.1% of ^{13}C . The IRMPD of CF_2Cl_2 , CF_3X ($\text{X}=\text{Cl}$, Br , or I), and CF_2HCl has been extensively studied with the intention of ^{13}C separation; most of the studies have been succinctly reviewed in the introductory section of the paper by Outhouse et al.⁶⁾ The IRMPD of CF_3Br was found to produce C_2F_6 with a ^{13}C content of 80%, and that of CF_2HCl to produce C_2F_4 with 90—96% under selected irradiation conditions.⁷⁻⁹⁾ However, the enrichment of ^{13}C above 70% is attainable only with a great sacrifice of the yield. Outhouse et al. have demonstrated production rates of 0.23 g h^{-1} for 50% ^{13}C and of 0.011 g h^{-1} for 72% ^{13}C using a high power CO_2 TEA laser (10 J, 10 Hz)⁶⁾. Therefore, there is general agreement that practical ^{13}C separation requires a two-stage process. For example, the first process is intended to increase a ^{13}C content from 1.1% to 20—50% (enrichment factor, 23—90) and the following second process is the production of ^{13}C above 90% (enrichment factor, 9—36). Since a high selectivity is not needed in each step, one can obtain a relatively large production rate of ^{13}C by such a two-stage process.

Abdushelishvili et al. have proposed the IRMPD of CF_3Br or CF_3I in the presence of NO , where NO scavenged CF_3 radicals produced from the first ^{13}C -selective IRMPD.¹⁰⁾ The resulting product, i.e.,

CF_3NO was presumed to be converted into CF_3Br or CF_3I for the second IRMPD, where the chemical conversion could be easily achieved by heating CF_3NO in Br_2 or I_2 vapor. Arai and his coworkers found that the IRMPD of C_2F_6 in the presence of Br_2 formed CF_3Br with 20—30% ^{13}C .¹¹⁾ The further IRMPD of the enriched CF_3Br resulted in the production of C_2F_6 with 90% ^{13}C . On the other hand, Hackett et al. showed that the production of C_2F_4 with 95—99% ^{13}C from equimolar mixtures of 50% $^{12}\text{CF}_2\text{HCl}$ and 50% $^{13}\text{CF}_2\text{HCl}$ was very efficient in energy expenditure.^{6,12)} They predicted the production rate of 1.7 g h^{-1} for 99% ^{13}C , assuming that equimolar mixtures were irradiated in a flow system with 10 J pulses at a repetition rate of 10 Hz. However, enriched CF_2HCl must be provided from other enrichment process. Recently, Ma et al. proposed the two-stage IRMPD of $\text{CF}_2\text{Cl}_2\text{-HI}$ or $\text{CF}_2\text{ClBr-HI}$ mixtures, where the first process was the production of CF_2HCl with ^{13}C content of 30% and the second process was the further enrichment by the selective decomposition of the CF_2HCl .¹³⁾ In view of the efficient decomposition of CF_2ClBr at low fluences, the IRMPD of $\text{CF}_2\text{ClBr-HI}$ mixtures could be one of the most effective two-stage processes to the practical enrichment of ^{13}C .

IRMPD of several fluorocarbons has been examined in our group for the development of a practical two-stage ^{13}C enrichment. In the course of the study we found that NH_3 significantly enhanced the decomposition yield in the IRMPD of CF_2HCl . The effect could be applied to an improvement of a ^{13}C yield in separation processes involving IRMPD of CF_2HCl . The present paper describes detailed experimental results and decomposition mechanisms.

Experimental

The experimental apparatus and procedures are essentially the same as were described elsewhere.^{14,15)}

Laser beams from a Lumonics 103-2 CO_2 TEA laser were focussed on the center of a reaction cell by a BaF_2 lens with a focal length of 60 cm, where the resulting focus area was about 0.045 cm^2 . The laser was operated without nitrogen gas at a repetition rate of 0.7 Hz. A typical pulse had a half width of about 80 ns and a triangle profile without a tail.

Output energies were measured with a Scientech 362 energy power meter and a Scientech 360001 detector. The reaction cell was a 113 cm long and 2.0 cm diameter cylindrical Pyrex tube equipped with KBr windows at both ends. In addition, the cell has KBr side windows for infrared spectrophotometric analysis, where the optical path length was 5.0 cm. The total volume was 393 cm³.

Formation amounts and isotopic compositions of products were determined by using a Shimadzu GC-7A gas chromatograph coupled with a NEVA quadrupole mass spectrometer, where a 3 mm ϕ and 3 m long VZ-10 column was mainly employed under programmed temperature variations. CF₂HCl purchased from Nitto Fluorochemical Co. was distilled repeatedly at low temperatures and the middle fractions were used as irradiation samples. We could not detect impurities such as C₂F₄ and CF₃H except for a trace amount of CF₂Cl₂. NH₃ from Suzuki Shokan Co. was also distilled repeatedly at low temperatures.

Results

The infrared absorption spectra of natural CF₂HCl and NH₃ are shown in Fig. 1. The bands centered at 1105 and 1120 cm⁻¹ in CF₂HCl are assigned to CF₂ symmetric and antisymmetric stretching vibration modes, respectively. The bands at 932 and 968 cm⁻¹ in NH₃ are due to degenerate symmetric deformation modes, where their R branches are extending on the higher wavenumber side. A ¹³C isotope shift has been reported to be nearly 30 cm⁻¹ for CF₂HCl.¹⁶⁾ In comparison to usual infrared absorption spectra, the band shapes become broader and the peaks shift to the red side in multiple-photon absorption spectra, depending on a laser fluence. The previous study of the IRMPD of CF₂HCl has shown that the decomposition probability of ¹³C bearing molecules is considerably larger than that of ¹²C bearing molecules in a wavenumber region from 1030 cm⁻¹ to 1060 cm⁻¹.⁹⁾ Since this study was concerned with ¹³C enrichment, we employed mainly the 9P (20) line at 1046.85 cm⁻¹ and the 9P (22) line at 1045.02 cm⁻¹ for irradiation of the mixtures. Although NH₃ also absorbed some of the laser radiation, neat NH₃ did not decompose at all under the present irradiation conditions, probably because of insufficient fluences for decomposition of a simple four-atom molecule.¹⁷⁾

The IRMPD of neat CF₂HCl gives only C₂F₄ and HCl as stable final products; these are the same products as in homogeneous gas-phase thermolysis.^{18,19)} The addition of NH₃ causes the formation of a new product, which can be definitely identified as CF₃H on the basis of its retention time on gas chromatography, a peak wavenumber in infrared spectroscopy, and a cracking pattern in mass spectrometry. In addition, we observed thick deposition of a white solid on the cell walls. The element analysis of the solid showed C, 1.04; H, 7.39; N, 25.7% in weight; the composition was consistent with NH₄Cl. No fluorocarbons containing Cl, (for example, CFH₂Cl, CFHCl₂, C₂F₂Cl₂) were detected on gas chromatography.

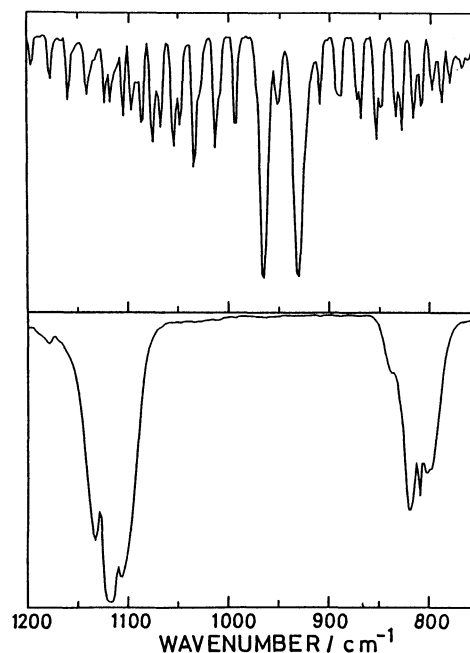


Fig. 1. Infrared absorption spectra of CF₂HCl (lower) and NH₃ (upper).

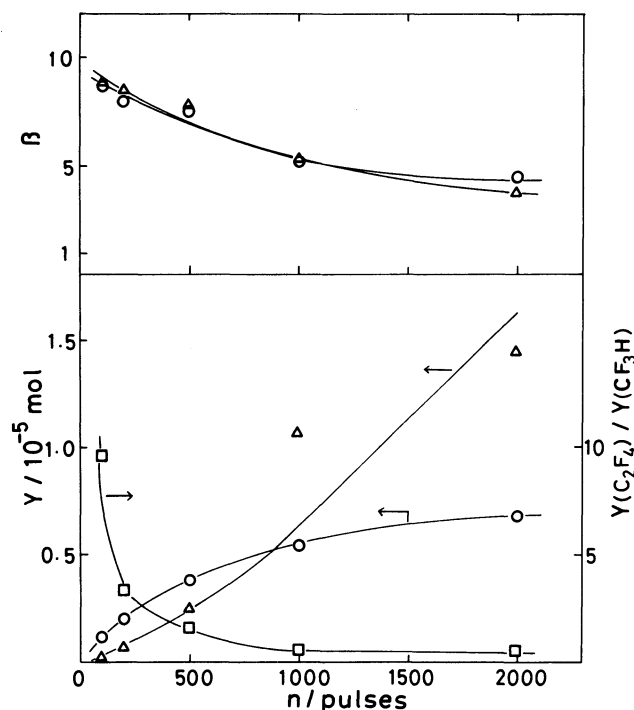


Fig. 2. Effects of pulse number n on yields Y (lower) and enrichment factors β (upper) for IRMPD of CF₂HCl-NH₃ mixtures at 5 Torr and 5 Torr. $\circ$, $Y(\text{C}_2\text{F}_4)$ or $\beta(\text{C}_2\text{F}_4)$; Δ , $Y(\text{CF}_3\text{H})$ or $\beta(\text{CF}_3\text{H})$; $\square$, $Y(\text{C}_2\text{F}_4)/Y(\text{CF}_3\text{H})$. Laser wavenumber, 1046.85 cm⁻¹; laser fluence at focus, about 27 J cm⁻².

Figure 2 shows the effects of pulse number on yields and enrichment factors for the IRMPD of CF₂HCl-NH₃ mixtures at 5 Torr plus 5 Torr (1 Torr=133.322 Pa). The yield for C₂F₄, $Y(\text{C}_2\text{F}_4)$ is defined as a total amount of C₂F₄ produced, while that for CF₃H,

$Y(\text{CF}_3\text{H})$ has a similar definition. The enrichment factors for C_2F_4 and CF_3H are as follows.

$$\beta(\text{C}_2\text{F}_4) = \{[^{13}\text{C}]/[^{12}\text{C}] \text{ in } \text{C}_2\text{F}_4\} / \{[^{13}\text{C}]/[^{12}\text{C}] \text{ in natural}\}$$

$$\beta(\text{CF}_3\text{H}) = \{[^{13}\text{C}]/[^{12}\text{C}] \text{ in } \text{CF}_3\text{H}\} / \{[^{13}\text{C}]/[^{12}\text{C}] \text{ in natural}\}$$

Ratios of $[^{13}\text{C}]$ to $[^{12}\text{C}]$ in C_2F_4 were determined from ion intensities of $^{12}\text{CF}_2^+$ at $m/z=50$ and those of $^{13}\text{CF}_2^+$ at $m/z=51$ for the C_2F_4 peak in GC-MS. On the other hand, we obtained similar ratios in CF_3H from ion intensities at $m/z=50$ ($^{12}\text{CF}_2^+$), $m/z=51$ ($^{12}\text{CF}_2\text{H}^+$ and

$^{13}\text{CF}_2^+$), and $m/z=52$ ($^{13}\text{CF}_2\text{H}^+$), taking the cracking pattern of CF_3H into consideration. Figure 2 includes plots of $Y(\text{C}_2\text{F}_4)/Y(\text{CF}_3\text{H})$ vs. number of pulses. $Y(\text{C}_2\text{F}_4)$ predominates over $Y(\text{CF}_3\text{H})$ at small pulse numbers, but $Y(\text{C}_2\text{F}_4)$ decreases to about a half of $Y(\text{CF}_3\text{H})$ at 2000 pulses. For pulse numbers less than 1000, logarithmic plots of $[\text{CF}_2\text{HCl}]_n/[\text{CF}_2\text{HCl}]_0$ vs. number of pulses give a good straight line, as shown in Fig. 3, where $[\text{CF}_2\text{HCl}]_0$ and $[\text{CF}_2\text{HCl}]_n$ are the amounts of CF_2HCl before and after n -pulse irradiation, respectively. The slope corresponds to a so-called specific decomposition rate in IRMPD, which is $2.1 \times 10^{-4} \text{ pulse}^{-1}$ in this case.

Figure 4 shows the laser line dependences of yields and enrichment factors for the IRMPD of 10 Torr CF_2HCl and 10 Torr NH_3 , where the number of laser pulses is 1000 at each line. In these irradiations, fluences at the focus were adjusted to fall within $20.8 \pm 2.8 \text{ J cm}^{-2}$ by inserting polyethylene films into the beam path. However, that for the 9P(34) line at 1033.49 cm^{-1} was 12.5 J cm^{-2} at a maximum output. Although $Y(\text{C}_2\text{F}_4)$ and $Y(\text{CF}_3\text{H})$ decrease with decreasing wavenumber, $\beta(\text{C}_2\text{F}_4)$ and $\beta(\text{CF}_3\text{H})$ have maxima at the 9P(26) line, i.e., 1041.28 cm^{-1} and the 9P(30) line, i.e., 1037.43 cm^{-1} . In addition, the parallel relations between C_2F_4 and CF_3H in yield and enrichment factor suggest that both compounds have the same origin, which must be a CF_2 radical produced in the ^{13}C selective IRMPD of mixtures. There seems to be a structure in the wavenumber dependences of $\beta(\text{C}_2\text{F}_4)$ and $\beta(\text{CF}_3\text{H})$. The structure may originate from the nar-

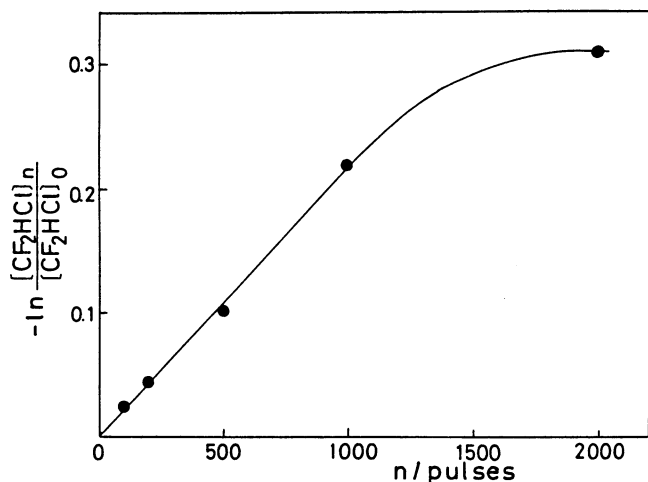


Fig. 3. Logarithmic plots of $[\text{CF}_2\text{HCl}]_n/[\text{CF}_2\text{HCl}]_0$ vs. number of pulses for IRMPD of CF_2HCl - NH_3 mixtures at 5 Torr and 5 Torr. $[\text{CF}_2\text{HCl}]_n$ and $[\text{CF}_2\text{HCl}]_0$, see text. Laser wavenumber, 1046.85 cm^{-1} ; laser fluence at focus, about 27 J cm^{-2} .

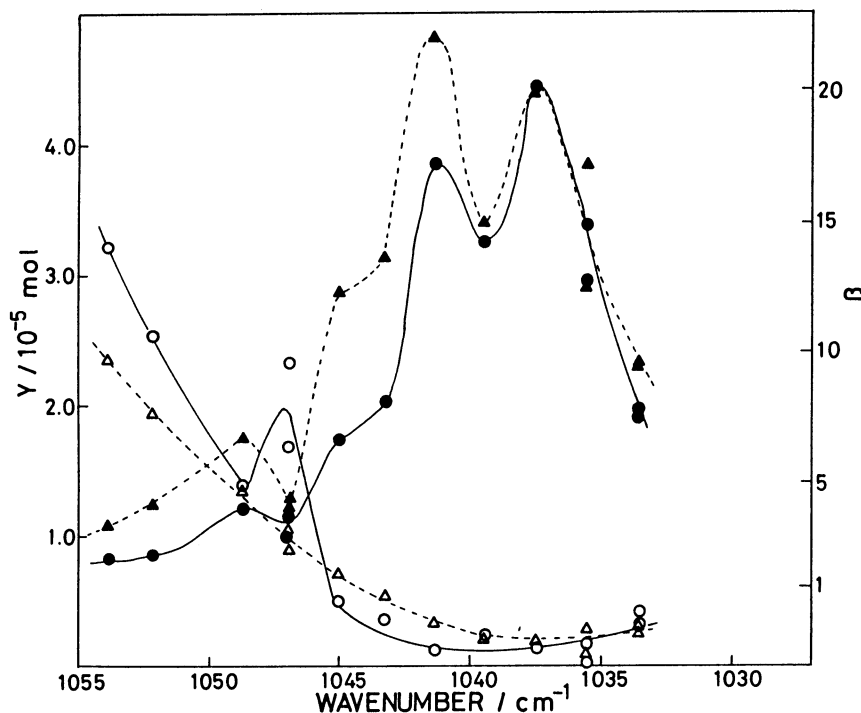


Fig. 4. Laser line dependences of yields Y and enrichment factors β for IRMPD of CF_2HCl - NH_3 mixtures at 10 Torr and 10 Torr. $\circ$, $Y(\text{C}_2\text{F}_4)$; $\triangle$, $Y(\text{CF}_3\text{H})$; $\bullet$, $\beta(\text{C}_2\text{F}_4)$; $\blacktriangle$, $\beta(\text{CF}_3\text{H})$; pulse number, 1000. Fluences, see text.

row resonance of the laser radiation with rotation-vibration transition energy in the discrete energy-level region.¹⁾ In the IRMPD of neat CF_2HCl for different irradiation frequencies at 1053.92, 1046.85, 1041.28, and 1035.47 cm^{-1} , the enrichment factor increased rapidly with decreasing wavenumber. We consider that a non-selective thermal process may contribute to the formation of both C_2F_4 and CF_3H in mixtures of 10 Torr CF_2HCl and 10 Torr NH_3 . The contribution becomes more significant with decreasing wavenumber, resulting in a rapid decrease in $\beta(\text{C}_2\text{F}_4)$ or $\beta(\text{CF}_3\text{H})$ below 1035 cm^{-1} .

In order to obtain standard data for comparison, we examined briefly the IRMPD of neat CF_2HCl under the same experimental conditions as the CF_2HCl - NH_3 mixtures. Figure 5 shows the pressure dependences of $Y(\text{C}_2\text{F}_4)$ and $\beta(\text{C}_2\text{F}_4)$, where the laser was adjusted to the 9P (22) line and the fluences were set at about 30 J cm^{-2} . As NH_3 is added to 1.0 Torr CF_2HCl , $Y(\text{C}_2\text{F}_4)$ decreases rapidly and, after passing through a minimum, increases gradually with increasing NH_3 (see Fig. 6). $Y(\text{CF}_3\text{H})$ increases simply with increasing NH_3 , while both $\beta(\text{C}_2\text{F}_4)$ and $\beta(\text{CF}_3\text{H})$ decrease. Hereafter, we define a total carbon yield, $Y(\text{C})$ as $2 Y(\text{C}_2\text{F}_4)$ for neat CF_2HCl or $Y(\text{CF}_3\text{H}) + 2 Y(\text{C}_2\text{F}_4)$ for

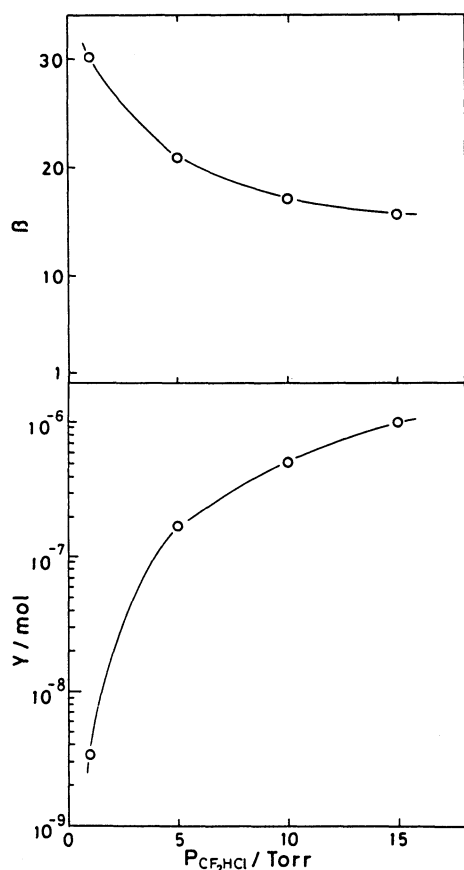


Fig. 5. Pressure dependences of $Y(\text{C}_2\text{F}_4)$ and $\beta(\text{C}_2\text{F}_4)$ for IRMPD of neat CF_2HCl . Laser wavenumber, 1045.02 cm^{-1} ; laser fluence at focus, about 29 J cm^{-2} ; pulse number, 1000.

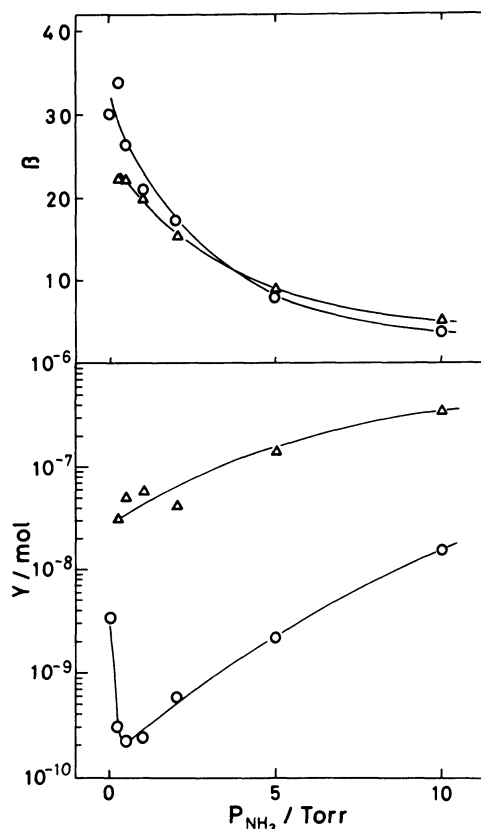


Fig. 6. Effects of NH_3 pressure on yields Y and enrichment factors β for IRMPD of CF_2HCl (1.0 Torr)- NH_3 mixtures. $\circ$, $Y(\text{C}_2\text{F}_4)$ or $\beta(\text{C}_2\text{F}_4)$; Δ , $Y(\text{CF}_3\text{H})$ or $\beta(\text{CF}_3\text{H})$. Laser wavenumber, 1045.02 cm^{-1} ; laser fluence at focus, about 29 J cm^{-2} ; pulse number, 1000.

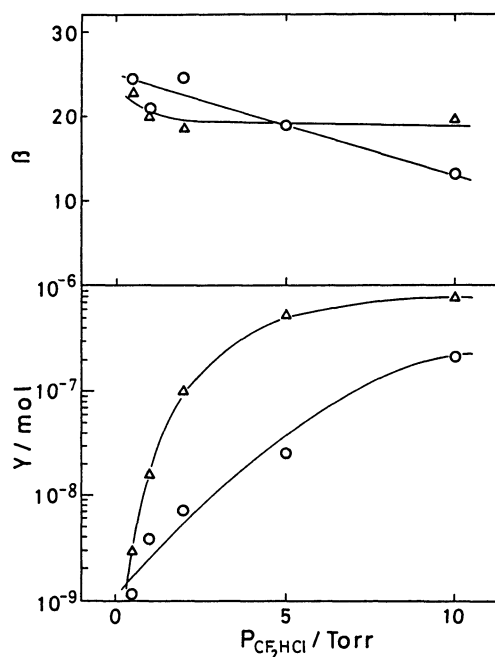


Fig. 7. Effects of CF_2HCl pressure on yields Y and enrichment factors β for IRMPD of CF_2HCl - NH_3 (1.0 Torr) mixtures. $\circ$, $Y(\text{C}_2\text{F}_4)$ or $\beta(\text{C}_2\text{F}_4)$; Δ , $Y(\text{CF}_3\text{H})$ or $\beta(\text{CF}_3\text{H})$. Laser wavenumber, 1045.02 cm^{-1} ; laser fluence at focus, about 29 J cm^{-2} ; pulse number, 1000.

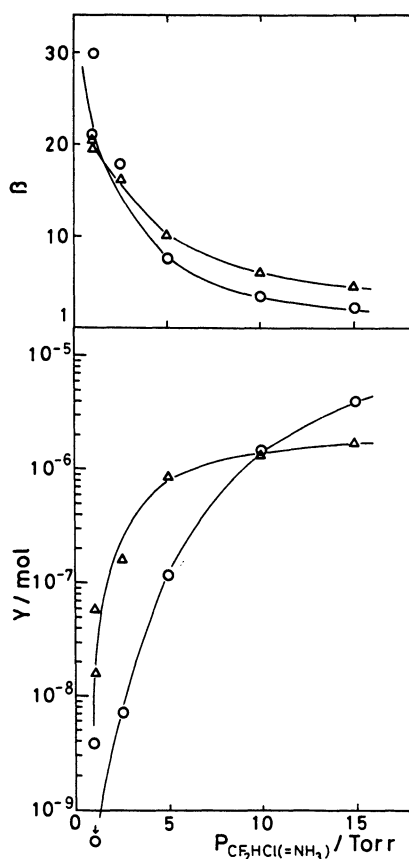


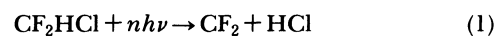
Fig. 8. Effects of total pressure on yields Y and enrichment factors β for IRMPD of equimolar CF₂HCl-NH₃ mixtures. O, $Y(\text{C}_2\text{F}_4)$ or $\beta(\text{C}_2\text{F}_4)$; Δ , $Y(\text{CF}_3\text{H})$ or $\beta(\text{CF}_3\text{H})$. Laser wavenumber, 1045.02 cm⁻¹; laser fluence at focus, about 28 J cm⁻²; pulse number, 1000.

mixtures. $Y(\text{C})$ for the mixture of 1.0 Torr CF₂HCl and 1.0 Torr NH₃ was found to be 5.8×10^{-7} mol, while $Y(\text{C})$ for 1.0 Torr neat CF₂HCl was only 6.8×10^{-8} mol; the former yield is about 8 times as large as the latter. The corresponding enrichment factors were $\beta(\text{CF}_3\text{H}) = 20$ for the mixture and $\beta(\text{C}_2\text{F}_4) = 30$ for the neat CF₂HCl.

Fluence effects on yields and enrichment factors were examined for mixtures of 1.0 Torr CF₂HCl and 5.0 Torr NH₃ in the range from 12 to 30 J cm⁻². For examples, $Y(\text{CF}_3\text{H})$ and $\beta(\text{CF}_3\text{H})$ at 12 J cm⁻² were 1.96×10^{-7} mol and 26, respectively, while those at 30 J cm⁻² were 1.40×10^{-6} mol and 9.0, respectively. $Y(\text{C}_2\text{F}_4)$ was much less than $Y(\text{CF}_3\text{H})$ at either fluence. An increase in fluence enhances product yields and reduces enrichment factors. When CF₂HCl was added to 1.0 Torr NH₃, we observed an increase in $Y(\text{C}_2\text{F}_4)$ or $Y(\text{CF}_3\text{H})$ and a decrease in $\beta(\text{C}_2\text{F}_4)$ or $\beta(\text{CF}_3\text{H})$ with increasing CF₂HCl, as shown in Fig. 7. Similar results were also obtained with total pressure effects on equimolar mixtures of CF₂HCl and NH₃, as shown in Fig. 8.

Discussion

The IRMPD of neat CF₂HCl has been explained satisfactorily in terms of the initial photochemical decomposition of CF₂HCl into CF₂ and HCl, and the subsequent combination between two carbene radicals.^{9,18)}



The same products, i.e., C₂F₄ and HCl have been obtained with the thermal decomposition of CF₂HCl, and the activation energy for the initial decomposition has been found to be 56 kcal mol⁻¹ (1 cal = 4.184 J) at pressures above 100 Torr.¹⁹⁾ Since the addition of HCl results in a decrease in decomposition rate, the following back reaction is considered to occur in thermolysis.



The heat of formation for CF₂, $\Delta H_f(\text{CF}_2)$ show large divergence among several determinations.^{19,20)} The enthalpy change of the initial decomposition is calculated to be 41 kcal mol⁻¹ on the basis of $\Delta H_f(\text{CF}_2) = -49.5$ kcal mol⁻¹.¹⁹⁾

In the presence of NH₃, one can consider the following bimolecular decomposition with an enthalpy change much less than that of Reaction 1.

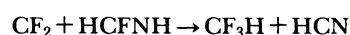


Therefore, the activation energy of Reaction 5 may be considerably smaller than the 56 kcal mol⁻¹ observed for Reaction 1. The reduction in activation energy means that a certain fraction of the excited molecules, which cannot decompose without NH₃, undergo Reaction 5 in the IRMPD of mixtures, where excited CF₂HCl originates from ¹³C-selective multiple-photon absorption. We conclude that the observed large increases in product yields are caused by the contribution of such excited parent molecules into laser-induced decomposition via Reaction 5.

The formation of C₂F₄ is explained simply by dimerization of two CF₂ radicals in mixtures. However, the rapid decrease of $Y(\text{C}_2\text{F}_4)$ by adding NH₃ suggests that CF₂ radicals react directly with NH₃ to form a key product, which is responsible for the formation of CF₃H via some subsequent process. The reaction and subsequent process may be as follows.



A further reaction of CF₂ with HCFNH will give CF₃H and HCN.



The relative yield of CF₃H to the yield of C₂F₄ tends to increase with increasing pulse number, as shown in

Table 1. IRMPD of CF₂HCl-NH₃ Mixtures

CF ₂ HCl Torr	NH ₃ torr	Pulse number	Fluence ^{a)} J cm ⁻²	Y(C ₂ F ₄)	Y(CF ₃ H)	β(C ₂ F ₄)	β(CF ₃ H)	Y(C) per pulse
1.0	0	1000	31	3.4×10 ⁻⁸	0	30	—	6.8×10 ⁻¹¹
1.0	1.0	200	25	4.2×10 ⁻⁸	Small	19	b)	4.2×10 ⁻¹⁰
5.0	0	1000	30	1.7×10 ⁻⁶	0	21	—	3.4×10 ⁻⁹
5.0	5.0	100	28	4.0×10 ⁻⁷	3.5×10 ⁻⁸	18	b)	8.4×10 ⁻⁹
10.0	0	1000	26	5.0×10 ⁻⁶	0	17	—	1.0×10 ⁻⁸
10.0	10.0	30	19	4.9×10 ⁻⁷	2.6×10 ⁻⁷	12	9	4.2×10 ⁻⁸
10.0	10.0	100	26	2.1×10 ⁻⁶	9.8×10 ⁻⁷	8	8	5.1×10 ⁻⁸
10.0	10.0	200	27	3.9×10 ⁻⁶	2.1×10 ⁻⁶	7	8	5.0×10 ⁻⁸

a) Fluence at focus. b) Selectivity could not be determined because of a small yield of CF₃H.

Fig. 2. This fact seems to indicate that the accumulation of a certain compound during pulse irradiation causes the observed preferential formation of CF₃H in a late period. However, we failed to detect directly HCF₂NH₂ by gas chromatography.

CF₂HCl is one of the most promising working molecules in ¹³C separation by IRMPD. Gauthier et al. have reported that the irradiation of 100 Torr natural CF₂HCl with the CO₂ laser radiation at 1046.9 cm⁻¹ and 3.5 J cm⁻² yields C₂F₄ containing 50% ¹³C at the efficiency that an absorption of 140 photons produces one carbon atom.⁹⁾ Therefore, a 100-watt CO₂ TEA laser can produce carbon at rate of 1.3 g h⁻¹, if 50% of the laser radiation is absorbed by CF₂HCl. Although the production rate is sufficiently high in their experiment, the ¹³C content must be increased to 90% or higher for practical purposes. In the previous paper we have proposed the two-stage IRMPD separation of ¹³C using CF₂Cl₂-HI and CF₂ClBr-HI mixtures, where the first IRMPD gives CF₂HCl with a ¹³C content of about 30% and the second IRMPD of the CF₂HCl is expected to result in the production of highly enriched ¹³C. Since CF₂ClBr decomposes at low laser fluences, one can obtain a relatively high yield of CF₂HCl in the CF₂ClBr-HI mixture. The production of 90% ¹³C from the CF₂HCl with a ¹³C content of about 30% corresponds to a separation process with an enrichment factor of only 21.

Table 1 tabulates yields and enrichment factors for the IRMPD of CF₂HCl in the presence of NH₃. The results clearly demonstrate that a total carbon yield per pulse increases significantly by adding NH₃ without a large loss of selectivity. The effect may be useful for the second stage in the IRMPD separation of ¹³C using a CF₂ClBr-HI mixture.

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