Appl. Phys. B 52, 266–272 (1991)

Applied Physics B Photophysics and Laser Chemistry

Enrichment of ^{13}C by IRMPD of CBr_2F_2

K. Sugita [1], **P. Ma** [2], **Y. Ishikawa** [3], **and S. Arai** [3]

[1] The Institute of Physical and Chemical Research, Wako-shi, Saitama 351-01, Japan
[2] Qinghai Institute of Saline Lakes, Academia Sinica, Xining, Qinghai, P.R. China
[3] Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan

Received 12 October 1990/Accepted 5 December 1990

Abstract. The CO_2-laser-induced infrared multiple photon decomposition of natural CBr_2F_2 in the presence of oxygen has been examined as a function of pulse number (30–1500), reactant pressures (CBr_2F_2, 10–150 Torr and O_2, 5–90 Torr), laser line [$9P(8) - 9P(32)$], and laser fluence (1–3 J cm^{-2}) to optimize irradiation conditions for ^{13}C-enrichment. CF_2O was the main carbon containing product and afterwards was converted into CO_2 via hydrolysis. A small amount of $C_2Br_2F_4$ was detected only under extreme conditions, for example, at high laser fluences or wavenumbers close to an absorption band. The ^{13}C-atom fraction of the final product CO_2 was found to be 20–80%, depending on experimental conditions. The two-stage IRMPD process proposed previously has been examined in further detail in the present study. First, CBr_2F_2 containing about 30% of ^{13}C was prepared in the ^{13}C-selective IRMPD of natural $CHClF_2$ in the presence of Br_2. The second-stage IRMPD of the CBr_2F_2 in the presence of oxygen under selected conditions resulted in the high enrichment of ^{13}C beyond 90%.

PACS: 82.50

Infrared multiple photon decomposition (IRMPD) of freon compounds has been extensively studied to elucidate fundamental multiple photon excitation and decomposition mechanisms as well as to develop a practical enrichment process of ^{13}C (natural abundance of ^{13}C, 1.1%) [1, 2]. Of a number of freon compounds examined, $CHClF_2$ shows a high decomposition yield and excellent ^{13}C-selectivity in IRMPD [2–4]. In the initial step of IRMPD, $CHClF_2$ decomposes into a CF_2 radical and a HCl molecule and, subsequently, two CF_2 radicals dimerize to form C_2F_4. The final product C_2F_4 has been found to have a ^{13}C-content of up to 96% under optimized experimental conditions. However, advanced studies have demonstrated that the enrichment of ^{13}C beyond 90% via single IRMPD process is energetically inefficient.

In previous papers we proposed an efficient two-stage IRMPD process, which consists of the ^{13}C-selective IRMPD of $CHClF_2$ in the presence of Br_2 and the subsequent IRMPD of CBr_2F_2 in the presence of O_2 [5, 6]. The CBr_2F_2 for the second stage was supplied from the first-stage IRMPD. The enrichment at the first stage was suppressed at 40% or less to obtain a sufficiently high yield rather than high selectivity. In the previous paper we have examined the first-stage enrichment, i.e., the IRMPD of $CHClF_2/Br_2$ mixtures under various conditions [6]. The present paper describes a detailed study of the second stage, i.e., the IRMPD of CBr_2F_2/O_2 mixtures, where CBr_2F_2 has either natural abundance or 30% atom fraction of ^{13}C. The observed results show that CBr_2F_2 decomposes at a high yield and high selectivity. In addition, the IRMPD of ^{13}C-enriched CBr_2F_2 easily produces CF_2O with a ^{13}C-atom content as high as 90%.

1. Experimental

The experimental apparatus and procedures are the same as previously described [5, 6]. A Lumonics 103 CO_2 TEA laser was operated at a repetition rate of 0.7 Hz using a mixture of He and CO_2 ($[He]/[CO_2] = 3/1$) as a lasing medium. The laser beam was truncated with a circular iris (diameter, 2.0 cm) and focused by a BaF_2 lens (focal length, 170 cm). The focal point has an area of 0.33 cm^2. The main part of the reaction cell consisted of two Pyrex glass tubes (inner diameter, 2.0 cm) connected together in a cross shape. KBr windows were attached to the four tube ends. The distance between windows along the direction of laser irradiation was 10 cm and that along the direction of infrared spectroscopy was 5 cm. The cell and photolysis volumes were 48.9 cm^3 and 3.3 cm^3, respectively. The reaction cell was placed in the vicinity of a focal point along the laser beam. The fluence distribution inside of the reaction cell can be regarded as uniform, because the cell length is much shorter than the focal length. The pulse energy was adjusted by inserting one or more polyethylene films into beam path. A Scientech 362 power meter with a Scientech 36001 detector was used to monitor an output of a laser pulse.

After laser irradiation, sample gases were passed through two traps cooled with liquid nitrogen, while oxygen was pumped out. The condensable portion was exposed to an excess of water vapor at room temperature. The water used was boiled sufficiently long to purge CO_2. The condensable portion, after drying with P_2O_5, was analyzed using a Shimadzu GC-7A gas chromatograph combined with a NEVA TE-150 quadrupole mass spectrometer. This portion consisted of CO_2, $C_2Br_2F_4$, and a large amount of unreacted CBr_2F_2. Isotopic compositions were determined for CO_2 flowing out from a gas chromatograph. The column was a 9 m Gasukuropack 55 (a porous styrene-divinylbenzene polymer; column diameter, 3 mm; column temperature, 140° C; a flow rate of He, $60\,\mathrm{ml\,min^{-1}}$).

CBr_2F_2 was purchased from PCR Research Chemicals Inc., and purified by low-temperature distillation.

2. Results and Discussion

We begin by explaining some technical terms used in this paper.

It has been generally accepted in IRMPD that the depletion of a decomposing molecule fits the following exponential equations:

$$[^{12}CBr_2F_2]_n = [^{12}CBr_2F_2]_0 \exp\{-(V_p/V_c)\,{}^{12}P_d n\}, \tag{1}$$

$$[^{13}CBr_2F_2]_n = [^{13}CBr_2F_2]_0 \exp\{-(V_p/V_c)\,{}^{13}P_d n\}. \tag{2}$$

$[^iCBr_2F_2]_0$ and $[^iCBr_2F_2]_n$ are partial pressures of $^iCBr_2F_2$ before and after the irradiation with n laser pulses, respectively, where i is the mass number of carbon and n is the pulse number. $V\!-\!c$ and $V\!-\!p$ are the volumes of a reaction cell and a laser photolysis zone, respectively. $^{12}P\!-\!d$ and $^{13}P\!-\!d$ are the so-called decomposition probabilities of $^{12}CBr_2F_2$ and $^{13}CBr_2F_2$, respectively. Selectivity S is defined as a ratio of $^{13}P-d$ to $^{12}P-d$. A content of ^{13}C in a product or a reactant is expressed by ^{13}C-atom fraction, $^{13}f(M) = 100 \times [^{13}C](\%)/([^{12}C] + [^{13}C])$, where M is either a product or a reactant. A relatively yield of CO_2, $Y(CO_2)$ is defined as $100 \times [CO_2](\%)/([CO_2] +$ [unreacted CBr_2F_2]). When an appreciable amount of $C_2Br_2F_4$ is produced, $Y(CO_2)$ is $100\times[CO_2](\%)/([CO_2]+$ $[C_2Br_2F_4]+$[unreacted CBr_2F_2]). The carbon-containing products observed for the IRMPD of CBr_2F_2/O_2 mixtures were mainly CF_2O and a trace of $C_2Br_2F_4$. The latter product was detected in the vigorous photolysis at the $9P(8)$ or $9P(12)$ line or at high fluences. CF_2O is easily converted into CO_2 via hydrolysis. The mechanism is as follows:

$$CBr_2F_2 + nh\nu \rightarrow CBrF_2 + Br \tag{3}$$

$$CBrF_2 + O_2 \rightarrow CF_2O + BrO \tag{4}$$

$$2\,BrO \rightarrow Br_2 + O_2 \tag{5}$$

$$2\,Br + M \rightarrow Br_2 + M \tag{6}$$

$$CF_2O + H_2O \rightarrow CO_2 + 2\,HF\,. \tag{7}$$

The isotope selectivity in the photophysical step (3) is brought into the final product CO_2.

2.1 *Effects of Pulse Number*

Figures 1 and 2 show effects of pulse number on $^{12}P_d$, $^{13}P_d$, S, $Y(CO_2)$, and $^{13}f(CO_2)$, where mixtures of 50 Torr

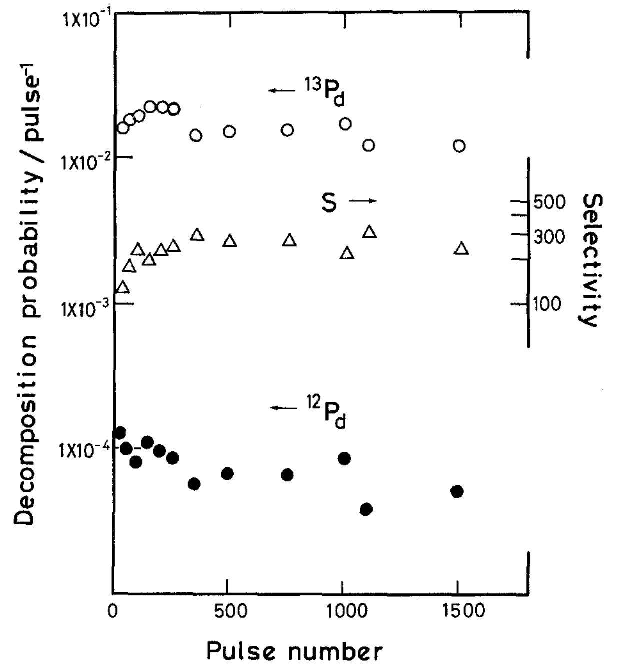

Fig. 1. Effects of pulse number on decomposition probabilities $^{12}P_d$ and $^{13}P_d$, and selectivity S. $P(CBr_2F_2)$, 50 Torr; $P(O_2)$, 10 Torr; laser line, $9P(28)$ at $1039.37\,\mathrm{cm^{-1}}$; fluence, $2.3\text{–}2.7\,\mathrm{J\,cm^{-2}}$

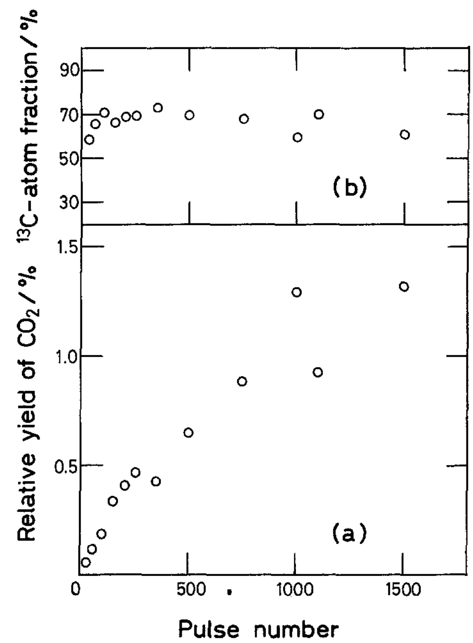

Fig. 2. Effects of pulse number on relative yield of CO_2, $Y(CO_2)$ (a) and ^{13}C-atom fraction of CO_2, $^{13}f(CO_2)$ (b). Experimental conditions same as Fig. 1

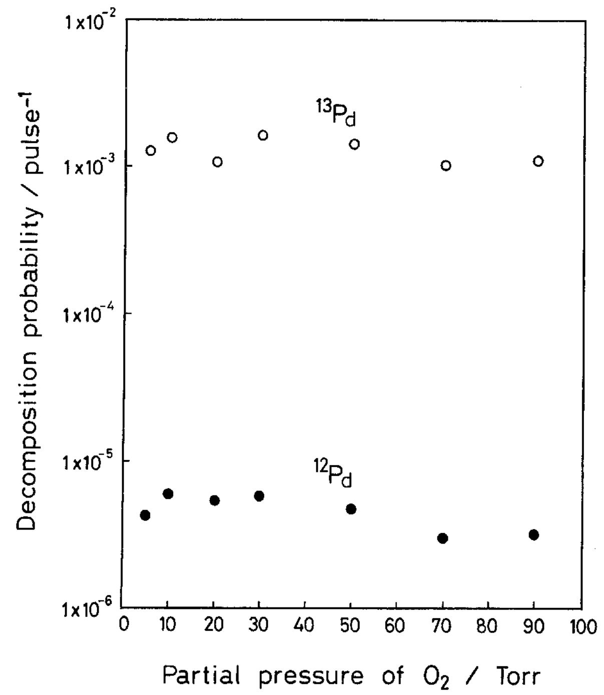

Fig. 3. Effects of partial pressure of O_2 on decomposition probabilities. $P(CBr_2F_2)$, 50 Torr; laser line $9P(28)$; fluence, 2.2–2.7 J cm^{-2}; pulse number, 500

CBr_2F_2 and 10 Torr O_2 were irradiated with the CO_2 laser radiation at 1039.37 cm^{-1}, i.e., the $9P(28)$ laser line and at fluences of 2.3–2.7 J cm^{-2}. When (1) and (2) hold over a wide range of pulse numbers, both decomposition probabilities should have constant values. However, there seems to be a tendency for $^{12}P_d$ and $^{13}P_d$ to decrease with increasing pulse number, although the plots are scattered. The decreases may be due to the back reaction between a $CBrF_2$ radical and accumulating Br_2, as the photolysis proceeds:

$$CBrF_2 + Br_2 \rightarrow CBr_2F_2 + Br\,. \qquad (8)$$

The back reaction should compete with reaction (4). The final product CO_2 has $^{13}f(CO_2)$ of 60–70% in this pulse number region.

2.2 Effects of O_2 *Pressure*

Effects of oxygen on the IRMPD of CBr_2F_2/O_2 mixtures are presented in Figs. 3 and 4. The partial pressure of oxygen $P(O_2)$ was varied from 5 Torr to 90 Torr, while that of CBr_2F_2 was 50 Torr in each mixture. The laser was tuned to the $9P(28)$ line and the fluence was in a narrow range of 2.3–2.7 J cm^{-2}. All the $CBrF_2$ radicals produced react with O_2 even at $P(O_2) = 5$ Torr, because the variation of $P(O_2)$ does not appreciably change $^{12}P_d$, $^{13}P_d$, $Y(CO_2)$, or $^{13}f(CO_2)$. The results also suggest that oxygen does not deactivate vibrationally excited CBr_2F_2 molecules during and after multiple photon excitation.

2.3 Effects of CBr_2F_2 *Pressure*

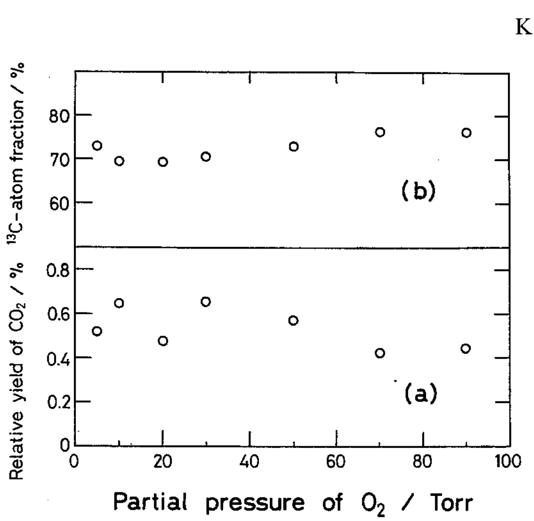

Fig. 4a, b. Effects of partial pressure of O_2 on relative yield of CO_2 (a) and ^{13}C-atom fraction of CO_2 (b). Experimental conditions same as Fig. 3

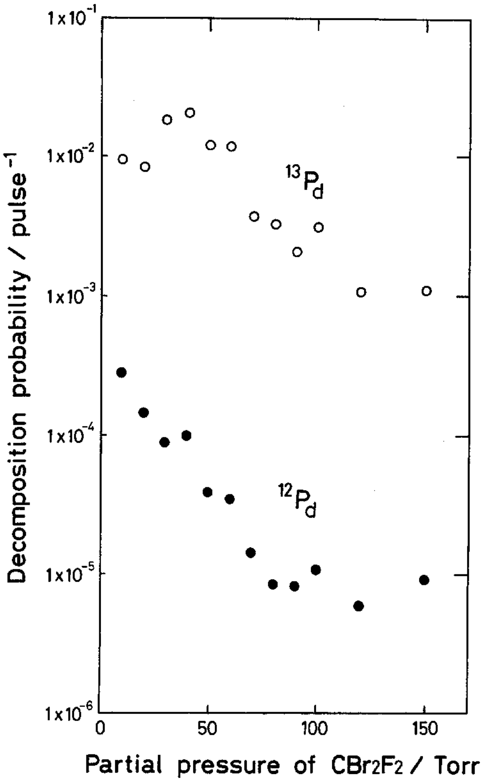

Fig. 5. Effects of partial pressure of CBr_2F_2 on decomposition probabilities. The ratio of $P(CBr_2F_2)$ to $P(O_2)$, 2:1; laser line, $9P(28)$; fluence, 2.3–2.5 J cm^{-2}; pulse number, 1000

Figures 5 and 6 present the effects of a partial pressure of CBr_2F_2, $P(CBr_2F_2)$ on the IRMPD of CBr_2F_2/O_2 mixtures, where the ratio of $[CBr_2F_2]_0$ to $[O_2]_0$ is always 2 : 1. Both decomposition probabilities decrease rapidly with increasing $P(CBr_2F_2)$ except for $^{13}P_d$ below 50 Torr, as shown in Fig. 5. This fact means that CBr_2F_2 itself deactivates highly vibrationally excited parent molecules very efficiently, because $P(O_2)$ does not affect $^{12}P_d$ and $^{13}P_d$.

$Y(CO_2)$ decreases very rapidly with increasing $P(CBr_2F_2)$ in parallel with $^{12}P_d$ and $^{13}P_d$. The ^{13}C-atom fraction of CO_2 increases with an increase in $P(CBr_2F_2)$,

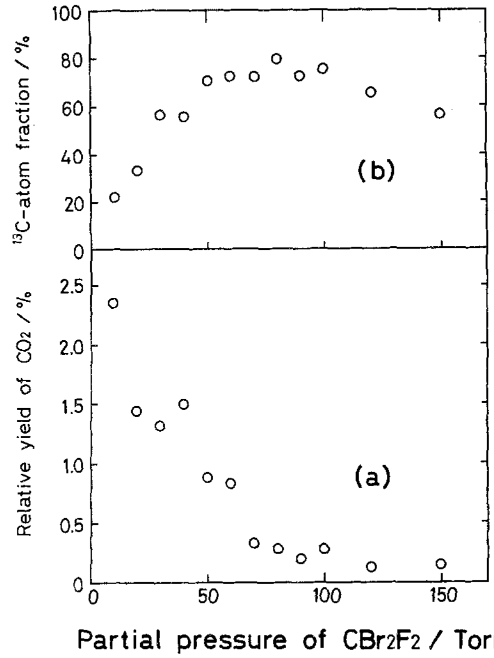

Fig. 6. Effects of partial pressure of CBr_2F_2 on relative yield of CO_2 (a) and ^{13}C-atom fraction of CO_2 (b). Experimental conditions same as Fig. 5

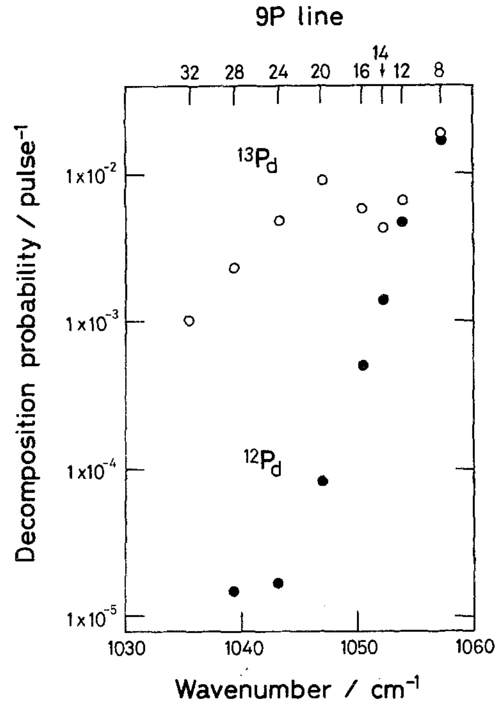

Fig. 7. Effects of laser wavenumber on decomposition probabilities. $P(CBr_2F_2)$, 50 Torr; $P(O_2)$, 30 Torr; fluence, 1.7–1.8 J cm^{-2}; pulse number, 500

and reaches a plateau value of about 70–80%. The slight decrease of $^{13}f(CO_2)$ at high pressures may be caused by the dilution of the product with the natural CO_2 contained in CBr_2F_2 as an impurity. The impurity contribution becomes larger at higher pressures because of diminishing $Y(CO_2)$.

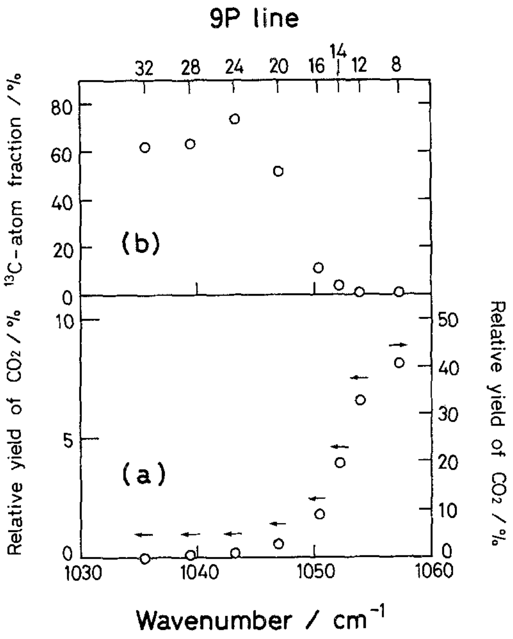

Fig. 8. Effects of laser wavenumber on relative yield of CO_2 (a) and ^{13}C-atom fraction of CO_2 (b). Relative yields of $C_2Br_2F_4$ were 5.2% at $9P(8)$ and 4.3% at $9P(12)$. Experimental conditions same as Fig. 7

2.4 *Effects of Laser Wavenumber*

Figure 7 shows laser wavenumber effects on $^{12}P_d$ and $^{13}P_d$, where mixtures of 50-Torr CBr_2F_2 and 30-Torr O_2 were irradiated with different laser lines at a fluence of 1.7–1.8 J cm^{-2}. $^{13}P_d$ has a shoulder at the $9P(20)$ line, while $^{12}P_d$ decreases very rapidly with decreasing wavenumber. However $^{13}f(CO_2)$ has the maximum value at $9P(24)$, as shown in Fig. 8. Although vigorous decomposition occurred at $9P(8)$ and $9P(12)$, no meaningful isotope selectivity was observed for the IRMPD at these lines. The significant formation of $C_2Br_2F_4$ suggests that $CBrF_2$ radicals are densely populated in the photolysis zone.

2.5 *Fluence Effects*

Figure 9 present fluence effects on $^{12}P_d$ and $^{13}P_d$. As generally observed for IRMPD, $^{12}P_d$ and $^{13}P_d$ increase with increasing fluence, while the selectivity decreases. However, $^{13}f(CO_2)$ at 1.4 J cm^{-2} is lower than that at 1.6 J cm^{-2} in Fig. 10. Since $Y(CO_2)$ decreases considerably with decreasing fluence and CBr_2F_2 contains a small amount of CO_2 as an impurity, the contribution due to the impurity may become larger at 1.4 J cm^{-2}, resulting in a decrease in $^{13}f(CO_2)$.

2.6 IRMPD *of* ^{13}*C-Enriched* CBr_2F_2

In the two-stage IRMPD process proposed previously for the high enrichment of ^{13}C, the first stage is the ^{13}C-

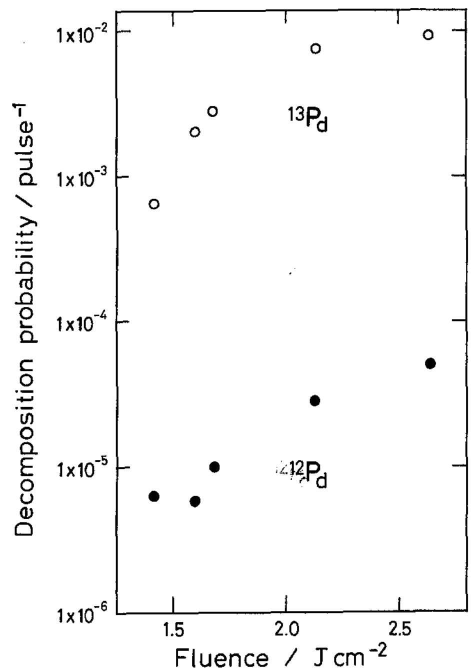

Fig. 9. Effects of laser fluence on decomposition probabilities. $P(CBr_2F_2)$, 50 Torr; $P(O_2)$, 30 Torr; laser line, 9P(28); pulse number, 1500

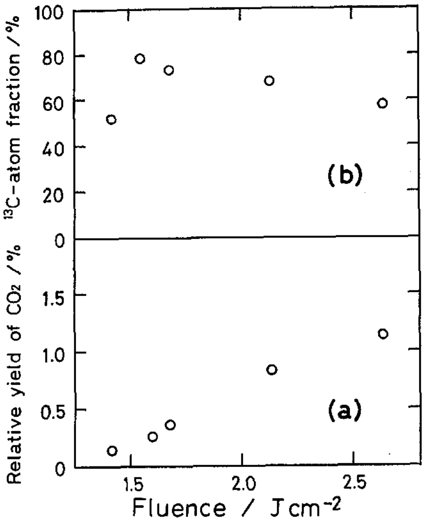

Fig. 10. Effects of laser fluence on relative yield of CO_2 (a) and ^{13}C-atom fraction of CO_2 (b). Experimental conditions same as Fig. 9

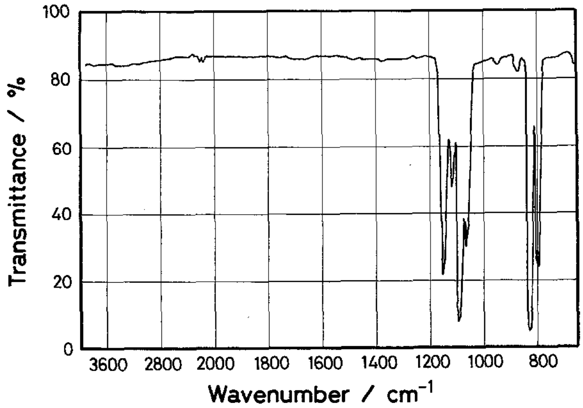

Fig. 11. Infrared absorption spectrum of ^{13}C-enriched CBr_2F_2. The scale above 2000 cm^{-1} is different from that below 2000 cm^{-1}

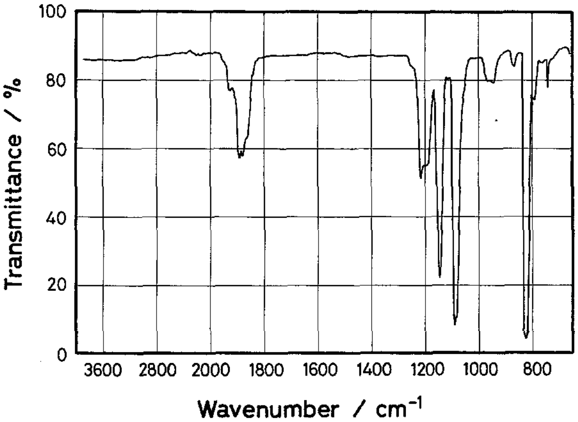

Fig. 12. Infrared absorption spectrum of irradiated ^{13}C-enriched CBr_2F_2 in the presence of O_2. $P(CBr_2F_2)$, 10 Torr; $P(O_2)$, 5 Torr; laser line, 9P(28); fluence, 2.2 J cm^{-2}; pulse number, 1500. The scale above 2000 cm^{-1} is different from that below 2000 cm^{-1}

selective IRMPD of natural $CHClF_2$ in the presence of Br_2 to form ^{13}C-enriched CBr_2F_2 [$^{13}f(CO_2) = 30$–40%] [5,6]. A relatively large amount of such enriched CBr_2F_2 was prepared using a large CO_2 laser and a flow reaction system. The irradiation cell was 3 m long cylindrical Pyrex tube (inner diameter, 3 cm), equipped with NaCl windows (diameter, 5 cm) at both ends. A Lumonics CO_2 822 TEA laser, one of the largest CO_2 lasers commercially available, was operated at an output of 8 J pulse^{-1} and at a repetition rate of 3 Hz. The mixture of $CHClF_2$ and Br_2 ($[CHClF_2]/[Br_2] = 2.0$) flowed into the cell at a total pressure of 100 Torr. The flow rates were 0.8 l min^{-1} for $CHClF_2$ and 0.4 l min^{-1} for Br_2 (at 760 Torr and room temperature). The laser beam was focused into a center of a reaction cell by a BaF_2 lens with a focal length of 2.1 m; the focal point has an area of 1.0 cm^2. The line used was 9P(22) at 1045.02 cm^{-1}. CBr_2F_2 [$^{13}f(CBr_2F_2) = 29.6\%$] was produced at a rate of 8.1 mmol h^{-1} (total amount, about 40 mmol) under these conditions.

Figure 11 shows the infrared absorption spectrum of the CBr_2F_2. The peaks at 830, 1090, and 1150 cm^{-1} are due to $^{12}CBr_2F_2$ while those shifted to the lower energy side by 24 cm^{-1} are due to $^{13}CBr_2F_2$. Since plentiful samples were not available, we have examined the second-stage enrichment of the CBr_2F_2 using a small CO_2 TEA laser and a 10-cm long reaction cell. The laser was tuned to the 9P(28) line at 1039.37 cm^{-1}. Figure 12 shows the infrared absorption spectrum after photolysis, where a mixture of 10-Torr CBr_2F_2 and 5-Torr O_2 was irradiated with 1500 pulses at a fluence of 2.0 J cm^{-2}. The comparison between the spectra before and after irradiation indicates that $^{13}CBr_2F_2$ decomposes selectively under the present conditions. The bands due to $^{12}CBr_2F_2$ do not decrease in intensity. The new bands at 940, 1210, and 1890 cm^{-1} are ascribed to $^{13}CF_2O$ [11]. The small shoulders at 1250 and 1930 cm^{-1} are ascribed to the other isotopic molecule $^{12}CF_2O$. We could estimate conversion yields of $^{13}CBr_2F_2$ from infrared absorption spectra before and after laser irradiation as well as from the amounts of $^{12}CO_2$ and $^{13}CO_2$ after the hydrolysis of $^{12}CF_2O$ and $^{13}CF_2O$. The results on the second-stage IRMPD are summarized in Table 1. A small amount of

Table 1. IRMPD of ^{13}C-enriched CBr_2F_2/O_2 mixtures [a]

$P(CBr_2F_2)$ [Torr]	$P(O_2)$ [Torr]	Ø [b] [J cm^{-2}]	n [c]	$^{12}P_d$ [pulse^{-1}]	$^{13}P_d$ [pulse^{-1}]	S [d]	$Y(CO_2)$ [%]	$^{13}f(CO_2)$ [%]
10 [e]	5	2.1	200	1.0×10^{-3}	4.1×10^{-2}	40	13	93
10	5	2.2	500	7.2×10^{-4}	3.0×10^{-2}	42	20	92
10	5	2.1	1000	4.2×10^{-4}	2.9×10^{-2}	69	27	93
10	5	2.2	1500	4.1×10^{-4}	2.6×10^{-2}	64	30	91
10	5	2.3	1500	4.1×10^{-4}	1.4×10^{-2}	35	25	89
2	1	2.1	200	9.8×10^{-4}	3.2×10^{-2}	33	11	92
4	2	2.0	200	1.1×10^{-3}	3.6×10^{-2}	34	12	92
7	3.5	2.0	200	1.4×10^{-3}	4.4×10^{-2}	31	14	91
10 [e]	5	2.1	200	1.0×10^{-3}	4.1×10^{-2}	40	13	93
10 [e]	5	2.1	200	1.0×10^{-3}	4.1×10^{-2}	40	13	93
10	5	1.6	200	6.2×10^{-4}	2.7×10^{-2}	44	9.3	94
10	5	1.3	200	3.3×10^{-4}	8.3×10^{-2}	25	3.3	91
30	15	1.5	200	5.6×10^{-3}	2.1×10^{-2}	3.8	12	59

[a] Laser line, $9P(28)$ at 1039.37 cm^{-1}
[b] Ø, fluence
[c] n, pulse number
[d] S, selectivity
[e] Same run

$C_2Br_2F_4$ was detected in each sample. However, the compound may not be produced photochemically, because enriched CBr_2F_2 contains $C_2Br_2F_4$ as an impurity. The isotope selectivity apparently decreases at higher fluences. Therefore, the fluence was set at about 2 J cm^{-2} or less. $P(O_2)$ and $P(CBr_2F_2)$ were 5 and 10 Torr, respectively. When $P(CBr_2F_2)$ exceeded 10 Torr, $^{13}f(CO_2)$ was lower than 90%.

2.7 *Comparison of* CBr_2F_2/O_2 *and* $CHClF_2/Br_2$

In the IRMPD of a natural CBr_2F_2/O_2 mixture we obtained a large decomposition yield and a high ^{13}C-selectivity, the values of which are comparable to those for a $CHClF_2/Br_2$ mixture. Typical results for these systems are presented in Table 2. Since product yields and ^{13}C-atom fractions depend strongly on a number of experimental parameters, it is difficult to obtain reproducible results. We found similar values for the yield of $^{13}CBr_2F_2$ per pulse ($CHClF_2/Br_2$) and for the yield of $^{13}CO_2$ per pulse (CBr_2F_2/O_2), as shown in the last column of Table 2. We have irradiated CBr_2F_2/O_2 mixtures with the $9P(24)$ line, which gave the maximum $^{13}f(CO_2)$ in Fig. 8b. The decomposition fluence for CBr_2F_2 is considerably lower than that for $CHClF_2$. This fact means a larger photolysis volume for CBr_2F_2/O_2 than $CHClF_2/Br_2$ in a focused irradiation geometry and, therefore, a higher product yield in CBr_2F_2/O_2.

The present study demonstrates that CBr_2F_2 is one of the most promising candidated for the efficient enrichment of ^{13}C by means of IRMPD. However, CBr_2F_2 has the disadvantage that the price is higher than that of $CHClF_2$. Our previous studies have already suggested some two-stage IRMPD processes starting from natural CBr_2F_2 and leading to high enrichment of ^{13}C [7–10]. The CO_2 laser irradiation of CBr_2F_2 in the presence of HI results in the production of ^{13}C-enriched $CHBrF_2$ in the first stage and the subsequent decomposition of the $CHBrF_2$ to form CH_2F_2 as a final product in the second stage. The two-stage ^{13}C-selective IRMPD occurs in a single irradiation procedure at the same laser wavenumber and fluence. The other process consists of the first IRMPD of a CBr_2F_2/Cl_2 mixture to give ^{13}C-enriched $CBrClF_2$ and the second IRMPD of the $CBrClF_2$ in the presence of O_2.

Table 2. Comparison between CBr_2F_2/O_2 and $CHClF_2/Br_2$ mixtures

Mixture [Torr]	Laser line	Ø [J cm^{-2}]	n	Y (product) [a] [%]	^{13}f (product) [a] [%]	y (^{13}product) [b] [% pulse^{-1}]
CBr_2F_2 50 O_2 25	$9P(24)$	2.6	150	0.53	58	2.0×10^{-3}
CBr_2F_2 50 O_2 25	$9P(24)$	2.6	200	0.98	39	1.9×10^{-3}
$CHClF_2$ 50 Br_2 5	$9P(22)$	3.6	100	0.49	44	2.2×10^{-3}

[a] The product for CBr_2F_2/O_2 is CO_2 and the product for $CHClF_2/Br_2$ is CBr_2F_2
[b] The relative yield of $^{13}CO_2$ per pulse for CBr_2F_2/O_2, and that of $^{13}CBr_2F_2$ for $CHClF_2/Br_2$. Y (product) × ^{13}f (product)/(100 × n)

Acknowledgements. The authors would like to express their thanks to Drs. Shohei Isomura and Hayato Kaetsu of the Institute of Physical and Chemical Research for producing ^{13}C-enriched CBr_2F_2.

References

1. V.S. Letokhov: *Nonlinear Laser Chemistry*. Springer Ser. Chem. Phys. Vol. 22 (Springer, Berlin, Heidelberg 1983)
2. A. Outhouse, P. Lawrence, M. Gauthier, P.A. Hackett: Appl. Phys. B **36**, 63 (1985)
3. M. Gauthier, C.G. Cureton, P.A. Hackett, C. Willis: Appl. Phys. B **28**, 43 (1982)
4. M. Gauthier, A. Outhouse, Y. Ishikawa, K.O. Kutschke, P.A. Hackett: Appl. Phys. B **35**, 173 (1984)
5. S. Arai, K. Sugita, P.H. Ma, Y. Ishikawa, H. Kaetsu, S. Isomura: Chem. Phys. Lett. **151**, 516 (1988)
6. S. Arai, K. Sugita, P.H. Ma, Y. Ishikawa, H. Kaetsu, S. Isomura: Appl. Phys. B **48**, 427 (1989)
7. P.H. Ma, K. Sugita, S. Arai: Chem. Phys. Lett. **137**, 590 (1987)
8. P.H. Ma, K. Sugita, S. Arai: Appl. Phys. B **49**, 509 (1989)
9. P.H. Ma, K. Sugita, S. Arai: Appl. Phys. B **50**, 385 (1990)
10. P.H. Ma, K. Sugita, S. Arai: Appl. Phys. B **51**, 103 (1990)
11. A.H. Nielsen, T.G. Burke, P.J.H. Woltz, E.A. Jones: J. Chem. Phys. **20**, 596 (1952)
12. P.H. Ma, S. Arai: Chin. Sci. Bull. **35**, 14 (1990)