CO$_2$ LASER ISOTOPE SEPARATION OF TRITIUM WITH HEPTAFLUOROPROPANES (CF$_3$CF$_2$CTF$_2$ AND CF$_3$CTFCF$_3$)

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Summary

Tritium isotope separation was attempted by laser-induced multiphoton dissociation (MPD) of tritiated heptafluoropropanes CF$_3$CF$_2$CTF$_2$ (n-C$_3$TF$_7$) and CF$_3$CTFCF$_3$ (i-C$_3$TF$_7$) using a transversely excited atmospheric pressure CO$_2$ laser. The isotopically selective MPD of n-C$_3$TF$_7$ was expected at frequencies below the 10 μm region. The MPD spectrum of i-C$_3$TF$_7$ showed a maximum at about 1000 cm^{-1} where i-C$_3$HF$_7$ was almost transparent. The dissociation rate constant and isotopic selectivity were studied as a function of the sample pressure, the temperature and the irradiation geometry. The critical fluence for dissociation of i-C$_3$TF$_7$ was found to be as low as 9 J cm^{-2} at 10 R(30) (982.1 cm^{-1}), which is lower than those for tritiated trifluoromethane (CTF$_3$) and pentafluoroethane (C$_2$TF$_5$). High isotopic selectivities exceeding 1400 were attained with i-C$_3$TF$_7$–i-C$_3$HF$_7$ at 982.1 cm^{-1}. An extremely large hydrogen isotope exchange rate was observed between i-C$_3$HF$_7$ and tritiated water. These results indicate that i-C$_3$TF$_7$ can be used as one of the most promising molecules for laser isotope separation of tritium.

1. Introduction

IR-laser-induced multiphoton dissociation (IRMPD) has been extensively investigated for applications in laser isotope separation (LIS) [1 - 3]. Of the many isotopes studied so far for molecular LIS, tritium is a unique example of LIS of a radioactive isotope [4 - 11]. We have reported the successful LIS of tritium by using trifluoromethane-t (CTF$_3$) as a working molecule [4] and have investigated the dependence of the dissociation rate constant and the selectivity on the experimental parameters (*e.g.* the laser frequency, the pressure and the irradiation geometry) [5, 6]. We have also

extended our survey of candidate molecules for LIS of tritium towards halogenated ethanes and found pentafluoroethane-*t* (C_2TF_5) [7] and 2-chloro-1,1,1,2-tetrafluoroethane-*t* (CF_3CTClF) [8] as promising working molecules with much lower critical fluences than CTF_3. We also found that C_2TF_5 was suitable for tritium separation from deuterium [9]. The multi-channel dissociation kinetics of pentafluoroethane were studied extensively by means of a scavenging method [12].

Since the critical fluence tends to decrease with increases in the molecular complexity or in the multiphoton absorption efficiency [13], we extended our survey towards halogenated propanes. We report in this paper the first successful isotope separation of tritium with 1,1,1,2,2,3,3-hepta-fluoropropane-*t* (n-C_3TF_7) and 1,1,1,2,3,3,3-heptafluoropropane-*t* (i-C_3TF_7). The dependence of the dissociation rate constant and the isotopic selectivity on the laser frequency, the sample pressure, the irradiation geometry and the temperature was studied. The hydrogen exchange rate between heptafluoro-propane and tritiated water (HTO) is also discussed.

2. Experimental details

2.1. Preparation of materials

n-C_3HF_7 (boiling point, $-16\,°C$) was synthesized similarly to the per-fluoro olefins reported in ref. 14. An aqueous solution of n-C_3F_7COOH (PCR Inc.) was neutralized with NH_4OH, evaporated over a water bath and then dried in vacuum over P_2O_5. n-$C_3F_7COONH_4$ thus obtained was pyrolysed at $220\,°C$ under a nitrogen atmosphere to yield volatile n-C_3HF_7, which was passed through two aqueous KOH scrubbers, passed over P_2O_5 and then condensed in a cold trap in dry ice.

i-C_3HF_7 (boiling point, $-19\,°C$) was prepared by irradiating a gaseous mixture of i-C_3F_7I (PCR Inc.) at 50 Torr and HI at 500 Torr with a low pressure mercury lamp for several hours. After the i-C_3F_7I had been completely converted to i-C_3HF_7, the remaining HI and iodine were removed by passing through an aqueous NaOH solution.

The heptafluoropropanes thus synthesized were further purified with a preparative gas chromatograph to more than 99%. The heptafluoropropanes were tritiated by hydrogen isotope exchange with HTO (1 ml; 1 mCi) in the presence of NaOH (0.2 g) and $(CH_3)_2SO$ (1 ml). A small amount of C_3F_6 (about 1%) produced during the tritiation of i-C_3HF_7 was removed complete-ly by means of gas chromatography. Typical tritium concentrations in n-C_3TF_7–n-C_3HF_7 and i-C_3TF_7–i-C_3HF_7 were found to be 0.2 ppm (about 0.3 μCi ml^{-1}).

2.2. Irradiation and analysis

The laser irradiation procedures were similar to those reported previous-ly [4 - 9]. A transversely excited atmospheric pressure CO_2 laser (Lumonics 103-2) was used for irradiation with a lasing gas of helium and CO_2 (pulse

duration, about 100 ns). The shot-to-shot variation in the laser output was within 3%. A gaseous sample mixture (n-C_3TF_7–n-C_3HF_7 or i-C_3TF_7–i-C_3HF_7) was introduced into a Pyrex photolysis cell (20 mm in inner diameter; 100 or 450 mm in length) equipped with KCl windows. The sample was then irradiated with the laser pulses (0.5 Hz) which had been passed through an aperture (14 mm in diameter), attenuated with CaF_2 or BaF_2 flats and focused into the centre of the photolysis cell by means of a BaF_2 lens (75 or 370 mm in focal length). The irradiated sample was condensed once into an evacuated sample loop cooled at −196 °C and then analysed by means of a temperature-programmed radio-gas chromatograph equipped with a Porapak Q separation column (80 - 100 mesh; 5 mm in inner diameter; 3 m in length), a thermal conductivity detector (TCD) and an internal gas flow proportional counter. All the products (*e.g.* C_2F_4, C_2F_6 and C_2HF_5) were well separated from C_3TF_7 and C_3HF_7 under these analytical conditions. The determinations of C_3TF_7 and C_3HF_7 were reproducible to within 1.1% and 0.5% respectively.

3. Results and discussion

3.1. Hydrogen isotope exchange rate between C_3HF_7 and HTO

Tritiation of n-C_3HF_7 was conducted by stirring for several hours in an HTO–NaOH–$(CH_3)_2SO$ mixture kept at about 60 °C. The tritiation conditions are similar to those for CHF_3 and C_2HF_5, which required NaOH and $(CH_3)_2SO$ as base catalysts and a reaction temperature of about 50 - 70 °C because of their relatively high pK_a values [4 - 8]. In contrast, the tritiation of i-C_3HF_7 was attained readily within 1 h at room temperature. Furthermore, the hydrogen exchange reaction of i-C_3HF_7 proceeded even in the absence of $(CH_3)_2SO$ in the mixture, although more slowly than in the presence of $(CH_3)_2SO$ in the mixture. It has been reported that the hydrogen exchange in i-C_3HF_7–CH_3OD is about 10^5 times faster than that in CHF_3–CH_3OD or in $CF_3(CF_2)_5CHF_2$–CH_3OD [15]. The hydrogen atom attached to the secondary carbon in i-C_3HF_7 is expected to be more acidic and to be subject to more rapid exchange with water than that attached to the primary carbon in n-C_3HF_7.

3.2. Laser frequency dependence of dissociation rate constants and isotopic selectivities

In most irradiation experiments, the pulse number was typically fixed at 1800 and the conversion range of the major component, C_3HF_7, was kept to within 10%. The C_3TF_7 and C_3HF_7 concentrations were found to decrease in a pseudo-first-order fashion in this range. Therefore, the first-order dissociation rate constants d_T and d_H for C_3TF_7 and C_3HF_7 respectively can be given by

$$d_T = -\frac{1}{t} \ln(1 - X_T) \tag{1}$$

$$d_{\mathrm{H}} = -\frac{1}{t} \ln(1 - X_{\mathrm{H}}) \qquad (2)$$

where X_{T} and X_{H} are the conversions of C_3TF_7 and C_3HF_7 respectively, after t irradiation pulses. As is expected from such a tightly focused irradiation geometry [16, 17], the dissociation rate constants for C_3TF_7 and C_3HF_7 were found to be proportional to $E_0^{1.5}$, where E_0 is the pulse energy. The rate constants at different E_0 were adequately normalized according to such a relation.

Figure 1 shows the frequency dependence of the dissociation rate constants for $n\text{-}C_3TF_7$ and $n\text{-}C_3HF_7$ and the selectivity $S_{\mathrm{T-H}}$ $(= d_{\mathrm{T}}/d_{\mathrm{H}})$. The selective dissociation of $n\text{-}C_3TF_7$ was effected by the laser lines of the P branch of the 10.6 μm band (Fig. 1), where d_{H} and d_{T} decreased with decreases in the laser frequency but d_{T} increased slightly near 930 cm^{-1}. On the basis of the IR spectra of $n\text{-}C_3HF_7$ [18] and $n\text{-}C_3DF_7$, we may expect the maximum d_{T} to appear at or somewhat below 900 cm^{-1}. (The $n\text{-}C_3DF_7$ was synthesized via hydrogen isotope exchange of $n\text{-}C_3HF_7$ with deuterated reagents, D_2O, NaOD and $(CD_3)_2SO$. A new IR peak appeared at about 990 cm^{-1}.) Consequently, the maximum $S_{\mathrm{T-H}}$ was obtained at 10 P(38) (927.0 cm^{-1}), which is about the lowest frequency line emitted stably and efficiently at a pulse duration of 100 ns with this laser. The d_{H} value increased rapidly with increases in the laser frequency above 970 cm^{-1} approaching a very strong IR absorption peak of $n\text{-}C_3HF_7$ at about 1040 cm^{-1} [18]. Although d_{T} also increased with increases in the laser frequency, no selective dissociation of $n\text{-}C_3TF_7$ was observed in this frequency region. We believe the decomposition of $n\text{-}C_3TF_7$ in this region was enhanced by the
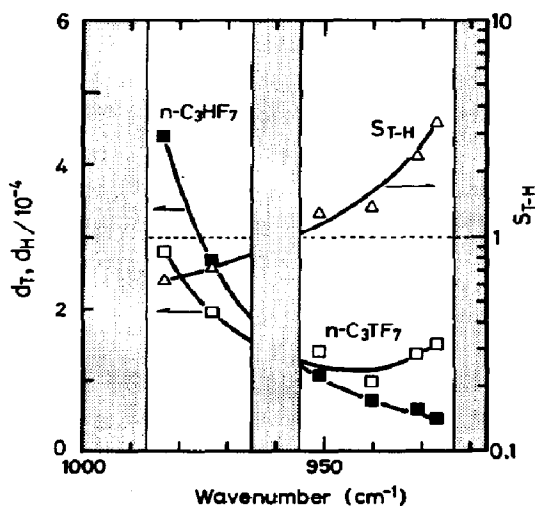

Fig. 1. Frequency dependence of the dissociation rate constants for $n\text{-}C_3TF_7$ (□) and $n\text{-}C_3HF_7$ (■) and of the selectivity $S_{\mathrm{T-H}}$ (△) ($n\text{-}C_3HF_7$ at 2 Torr containing 0.2 ppm $n\text{-}C_3TF_7$ at room temperature; pulse energy $E_0 = 0.36$ J; lens focal length, 75 mm). CO_2 laser lines are not available in the shaded regions.

collisional energy transfer from excited $n\text{-}C_3HF_7{}^*$ to $n\text{-}C_3TF_7$ as reported in the LIS of tritium with CTF_3 [5, 6]. Irradiation at higher frequencies (above 1000 cm^{-1}) was not promising, because $n\text{-}C_3HF_7$ has an extremely strong IR absorption at 1040 cm^{-1}; nearly non-selective dissociation of $n\text{-}C_3TF_7$ ($S_{T-H} \approx 1.2$) was observed at 9 R(14) (1074.6 cm^{-1}) with a large d_H value of about 16×10^{-4}. Since better selectivity was expected at frequencies lower than the 10 P lines of the CO_2 laser, lasers which can emit lower frequency light, such as an NH_3 laser [19], may be useful for tritium separation with the $n\text{-}C_3TF_7\text{-}n\text{-}C_3HF_7$ system. Since $n\text{-}C_3TF_7$ may not be a promising molecule with the CO_2 laser under these conditions, $i\text{-}C_3TF_7$ will be discussed in detail in this paper.

The frequency dependence of the dissociation rate constants for $i\text{-}C_3TF_7$ and $i\text{-}C_3HF_7$ is shown in Fig. 2. The multiphoton dissociation (MPD) spectrum of $i\text{-}C_3TF_7$ seems to have its maximum at around 1000 cm^{-1} where emission lines are not available with regular $^{12}CO_2$ lasers. As is anticipated from the IR spectrum of $i\text{-}C_3HF_7$, which has an absorption peak at 1130 cm^{-1} with a tailing towards the lower frequency region [18], d_H became large above 1050 cm^{-1} but very small at about 980 cm^{-1} where d_T was appreciably large. The d_H value increased slightly at much lower frequencies corresponding to the blue-side edge of the IR absorption peak of $i\text{-}C_3HF_7$ at about 910 cm^{-1} [18]. Consequently, the largest S_{T-H} value of 14.0 was obtained at 10 R(30) (982.1 cm^{-1}) under the tightly focused irradiation geometry. This value is comparable with or somewhat larger than those obtained under similar conditions in $CTF_3\text{-}CHF_3$ [4] and $C_2TF_5\text{-}C_2HF_5$ systems [7].
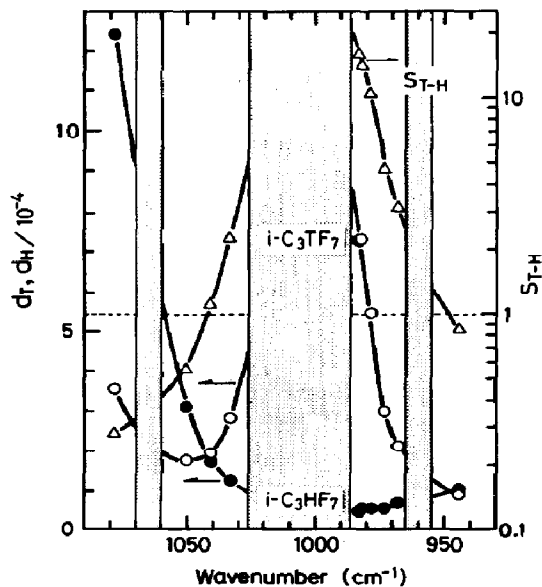

Fig. 2. Frequency dependence of the dissociation rate constants for $i\text{-}C_3TF_7$ ($\bigcirc$) and $i\text{-}C_3HF_7$ ($\bullet$) and of the selectivity S_{T-H} ($\triangle$) ($i\text{-}C_3HF_7$ at 2 Torr containing 0.2 ppm $i\text{-}C_3TF_7$ at room temperature; pulse energy $E_0 = 0.36$ J; lens focal length, 75 mm). CO_2 laser lines are not available in the shaded regions.

The value of the critical fluence Φ_c for complete dissociation can be approximately estimated by a simple threshold model under the tightly focused irradiation geometry. The Φ_c values obtained for CTF_3, C_2TF_5, n-C_3TF_7 and i-C_3TF_7 are listed in Table 1, together with the S_{T-H} values. i-C_3TF_7 shows the lowest Φ_c value of these fluorocarbons with appreciably high isotopic selectivity, while the irradiation was made at a wavenumber near the red-side edge of its MPD spectrum where the d_T value is less than the maximum. The irradiation at around 1000 cm^{-1} with a $^{13}CO_2$ laser [20] may attain the highest dissociation rate constant of i-C_3TF_7 and also the highest isotopic selectivity S_{T-H}.

TABLE 1

Critical fluences for dissociation of tritiated fluorocarbons and isotopic selectivities observed under the tightly focused irradiation geometry [a]

Molecule	Irradiation wavenumber (cm^{-1})	Critical fluence Φ_c (J cm^{-2})	Isotopic selectivity S_{T-H}	Reference
CTF_3	1074.6	80	12.5	[5]
C_2TF_5	944.2	19	9.0	[7]
n-C_3TF_7	927.0	25	3.4	This work
i-C_3TF_7	982.1	9	14.0	This work

[a] Pulse duration, 100 ns; sample pressure, 2 Torr; lens focal length, 75 mm.

3.3. Pressure effect

Figure 3 shows the pressure dependence of the dissociation rate constants for i-C_3TF_7 and i-C_3HF_7 and the selectivity at 10 R(30) (982.1 cm^{-1}). The d_T value decreased with increases in the pressure whereas d_H remained nearly unchanged. Consequently, S_{T-H} decreased from 24 at 0.2 Torr to 7 at 10 Torr. The collisional de-excitation of vibrationally excited i-$C_3TF_7^*$ by i-C_3HF_7 during and after the laser pulse may be responsible for the pressure dependence of d_T. This pressure dependence is similar to that observed in the C_2TF_5-C_2HF_5 system [7] and may be typical of the IRMPD of large molecules where collisions induce vibrational quenching. The enhancement of dissociation with increases in the pressure by collision-induced relaxation of rotational bottle-necking [13] (as observed in the CTF_3-CHF_3 system [5, 6]) was not observed in the i-C_3TF_7-i-C_3HF_7 system. The operating sample pressure will be improved by using a much shorter pulse duration CO_2 laser (e.g. about 2 ns) to reduce the collisional de-excitation during the laser pulses.

3.4. Effect of irradiation geometry and temperature

Under the tightly focused irradiation geometry (focal length, 75 mm), S_{T-H} is limited by the undesirable dissociation of i-C_3HF_7 because the focal

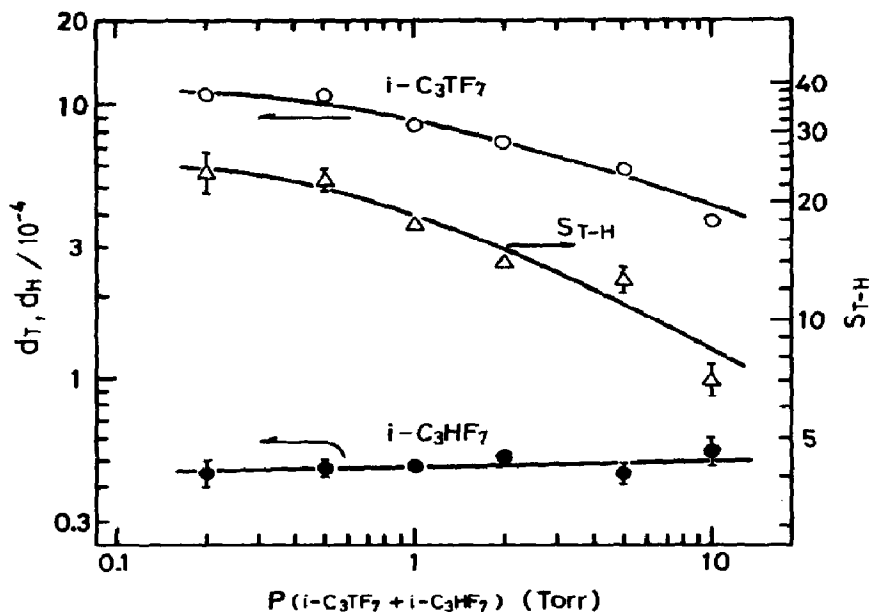Fig. 3. Pressure dependence of the dissociation rate constants for $i\text{-}C_3TF_7$ (○) and $i\text{-}C_3HF_7$ (●) and of the selectivity S_{T-H} (△) under a tightly focused irradiation geometry at room temperature (laser line, 10 R(30) (982.1 cm^{-1}); pulse energy E_0 = 0.36 J).

fluence is much larger than the Φ_c value for $i\text{-}C_3HF_7$. The dissociation of $i\text{-}C_3HF_7$ can be remarkably suppressed by reducing the focal fluence using a mildly focused irradiation geometry. Table 2 shows the results obtained by using a lens with a focal length of 370 mm. Irradiations were performed at 10 R(30) (982.1 cm^{-1}) and 9 P(34) (1033.5 cm^{-1}) corresponding respectively to the red-side and the blue-side edge of the MPD spectrum of $i\text{-}C_3TF_7$ (Fig. 2). The pulse energy was adjusted so that the focal fluence became slightly larger than the Φ_c value for $i\text{-}C_3TF_7$ at each line. Then S_{T-H} was improved remarkably. In particular, no measurable consumption of $i\text{-}C_3HF_7$ was observed after 1000 - 10 000 irradiation pulses at 10 R(30) (982.1 cm^{-1}). No dissociation product of $i\text{-}C_3HF_7$ (e.g. C_2F_4 or C_2HF_5) was observed above the detection limit of the TCD. Accordingly, the upper limit of d_H and thus the lower limit of S_{T-H} were estimated by considering the sensitivity of the TCD as follows. It has been confirmed in separate experiments that the peak areas of the irradiation products were proportional to X_H of $i\text{-}C_3HF_7$ within the conversion range between 1.5% and 5.5%. On the assumption that a linear correlation holds below this conversion range, X_H was estimated to be below 0.34% after 10 000 irradiation pulses, and hence d_H was estimated to be below 0.34×10^{-6}. The lower limit for S_{T-H} thus obtained was as large as 1400, and this molecule is a most promising candidate for tritium isotope separation.

The temperature effect was examined by cooling the photolysis cell in dry ice. The dissociation rate constant d_T for $i\text{-}C_3TF_7$ remained almost un-

TABLE 2

Tritium isotope separation with i-C_3TF_7 under a mildly focused irradiation geometry (focal length, 370 mm)

Wavenumber (cm^{-1})	Focal fluence Φ_f $(J\ cm^{-2})$	Pulse number	$1 - X_T$	$1 - X_H$	d_T $(\times 10^{-6})$	d_H $(\times 10^{-6})$	S_{T-H}
982.1	13.7	1000	0.616	—[a]	484	< 0.34[a]	> 1400[a]
1033.5	24.3	1000	0.760	0.944	274	58	4.7

[a] Since the conversion of i-C_3HF_7 was below the detection limit even after 10 000 irradiation pulses, the d_H and S_{T-H} values shown only represent the upper and lower limits respectively (see text).

changed at the blue-side edge of the MPD spectrum (1033.5 cm^{-1}), while d_T at the red-side edge (982.1 cm^{-1}) decreased to about one-half its value at lower temperatures. The decrease in d_T at lower temperatures at the lower frequency side can be explained in terms of the suppression of the hot-band absorption, since the ground state population of i-C_3TF_7 at 300 K is estimated to be of the order of 5×10^{-3}. A similar frequency dependence of the temperature effect has been reported in the IRMPD of SF_6 [21]. However, lowering the temperature caused a large decrease in d_H at 1033.5 cm^{-1}, increasing the S_{T-H} value from 4.7 to 18. Although the d_H value at 982.1 cm^{-1} is too small to be measured directly under the mildly focused irradiation geometry, it is also expected that lowering the temperature results in a similarly large decrease in d_H and hence an increase in S_{T-H} at 982.1 cm^{-1}. Such an improvement in the S_{T-H} value at lower temperatures would be most significant at around 1000 cm^{-1} where d_T has its maximum value.

4. Concluding remarks

The isotope separation of tritium by IRMPD of n-C_3TF_7 and i-C_3TF_7 was reported. The irradiation of an i-C_3TF_7–i-C_3HF_7 mixture (2 Torr) with a CO_2 laser at 10 R(30) (982.1 cm^{-1}) gave an appreciably low critical fluence (about 9 J cm^{-2}) for i-C_3TF_7 dissociation and an extremely high selectivity exceeding 1400. These values may be further improved by employing a $^{13}CO_2$ laser to irradiate at the MPD peak of i-C_3TF_7 or by utilizing a CO_2 laser with a short pulse duration to overcome the collisional de-excitation at higher sample pressures. The i-C_3TF_7–i-C_3HF_7 system showed an extremely large hydrogen isotope exchange rate with HTO, indicating an important practical advantage in the LIS cycle for tritium removal from water.

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