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Tritium Isotope Separation by CO_2-Laser Irradiation at Low Temperatures

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Abstract. Tritium isotope separation by CO_2-laser induced multiphoton dissociation of CTF_3 is investigated. For the optimization of the performance of this working substance, trifluoromethane, the conditions to yield high-selectivity at high-operating pressure and low-critical fluence for complete dissociation are studied using our deconvolution procedure. The irradiation conditions are varied over the following ranges; wavenumber: 1052–1087 cm^{-1}, gas temperature: 25 °C to −78 °C, CHF_3 pressure: 5–205 Torr. The selectivities exceeding 10^4 are observed for 85–205 Torr CHF_3 at −78 °C by the irradiation at 1057 cm^{-1}.

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As much as 2.5×10^4 Ci of tritium (^3H or T) is accumulated in spent nuclear fuel after the generation of 10^9 W·yr of electricity by typical nuclear reactors [1], and is released mainly at reprocessing plants.

The concern to control tritium effluent to the environment is fortified by the fact that tritium is very easily taken into living organisms in the form of tritiated water (HTO).

For the purpose of removal of tritium at the very low-level from the effluent of reprocessing plants, a development of a new tritium separation process is called for.

Laser-induced tritium isotope separation technique may be ideal for such an object, since the required energy for separation is directly related to the tritiated molecules present at very low-concentration levels while major untritiated molecules are left unaffected.

In 1979, our group [2] and the group at Lawrence Livermore National Laboratory (LLNL) [3] both performed the fundamental vibrational frequency analysis of halogenated methanes independently and reached the same conclusion that among tritiated halogenated methanes only tritiated trifluoromethane (CTF_3) has selective absorption in the CO_2-laser range.

Each group learned the effort of the other group after laser isotope separation of tritium was first published by our group [4]. The LLNL group measured the spectrum of synthesized CTF_3 [5] and confirmed the predicted absorption of CTF_3.

Although trifluoromethane had been reported as an excellent working substance for laser-induced deuterium separation [6], the use of this substance for tritium isotope separation was not straightforward, since the ν_5 absorption mode of CDF_3 at 970–980 cm^{-1} is estimated to shift away from the CO_2 laser range when it is tritiated. After the vibrational frequency analysis, it was revealed that a new ν_2 absorption of CTF_3 is located in the 9 μm range of a CO_2 laser.

Tritium isotope separation by CO_2-laser induced multiphoton dissociation of trifluoromethane has been intensively investigated by our group [7–10] since then. A selectivity – determining mechanism was revealed in the course of kinetic studies: the selectivity was controlled by the direct multiphoton dissociation of CHF_3 rather than V–V energy transfer from multiphoton excited CTF_3 to unexcited CHF_3.

The fact that CHF_3 dissociation was unaffected by CTF_3 dissociation was confirmed by two-experimental results: A 10^3-fold change of CTF_3 partial pressure does not affect the specific dissociation rates for both CHF_3 and CTF_3 [7], and a reduction of the gas temperature increased the selectivity and the operating pressure remarkably [10].

Newly developed deconvolution procedure [9, 11] was applied to the analysis of batch irradiation experiments. It was found that the relation between the selectivity and the operating pressure is controlled by two different mechanisms. At lower pressures, isotopically-selective slightly pressure-dependent process dominates, while it is overwhelmed by isotopically non-selective strongly pressure-dependent process at higher pressures. It was discussed in [9] that this process is neither due to simple gas-heating effect nor collision-induced dissociation of multiphoton excited molecules alone. The nature of this second process is still partly unknown. Needless to mention, this process is not related to gas breakdown. The advent of this process is controlled by pressure but not by fluence: even at the lowest fluence in the experiment the selectivity was found to be lost when the pressure is above a certain value. More detailed investigation of this process is expected to help understanding the role of collisions in multiphoton dissociation.

From a practical viewpoint, it is necessary to optimize the gas temperature and irradiation wavelength in order to obtain the best performance of this working substance, trifluoromethane. Three major criteria of such optimization are operating pressure, selectivity and critical fluence. While the selectivity should satisfy a certain requirement, increase of the operating pressure and decrease of the critical fluence are strongly required for the increase of the process treatment rate.

Although thorough optimization of the whole process should be done after the design of a new continuous photoreactor for tritium isotope separation, it is very useful at this stage to know how these criteria can be affected by controllable variables such as temperature and irradiation wavenumber.

1. Experiment

Preparation of the tritiated trifluoromethane was similar to the procedure previously reported [9].

The beam from a TEA-CO_2 laser (Lumonics 821) with long pulse duration (100 ns FWHM spike followed by ~1 μs tail) was focused by a BaF_2 lens (f.l. = 38 cm) into a Pyrex glass cell (45 cm in length, 2 cm in diameter) equipped with a glass circulation pump to avoid incomplete mixing at high-pressures.

The cell was placed in a thermally insulated box packed with crushed dry ice or filled with coolant slush while the KBr windows and the circulation pump were kept at the room-temperature. The temperature of the reaction region near the focal spot (~20 cm in length) was kept at −78 °C with dry ice or at −47 °C with *m*-xylene slush. A heat-exchange section was inserted between the pump placed at the room-temperature and the cell immersed in the coolant.

The depletions of CHF_3 and CTF_3 were measured with a thermal-conductivity detector and a proportional counter, respectively, after the gas chromatographic separation (Porapak Q).

2. Deconvolution

Our deconvolution procedure was explained previously [9]. Briefly, the pulse energy (E_0) dependence of the specific dissociation rate b [$\equiv -\ln(1-X)/t$, X being the fraction dissociated after t pulse irradiation] is converted to the fluence (Φ) dependence of the fractional conversion per pulse (q) as follows. The relation between q and Φ is assumed to be expressed as

$$q=(\Phi/\Phi_c)^n \quad \text{for} \quad \Phi<\Phi_c, \tag{1a}$$

$$q=1 \quad \text{for} \quad \Phi\geqq\Phi_c. \tag{1b}$$

The beam envelope is given by

$$r^2=r_f^2(1+Z^2/a^2). \tag{2}$$

The value n of (1a) is determined as the slope of the $\log b$ vs. $\log E_0$ plot in the low-pulse energy region. With the experimentally determined dimensionless reaction volume Y ($\equiv bV_{cell}/V_f$, V_{cell}: cell volume, V_f: focal volume), the dimensionless fluence F ($\equiv \Phi/\Phi_c$, Φ_c: critical fluence) is calculated as

$$Y=\Theta\cdot F^n \quad \text{for} \quad F<1, \tag{3}$$

$$\Theta=\int_0^{L/a}(1+k^2)^{1-n}dk, \tag{4}$$

$$Y=(F-1)^{1/2}+\tfrac{1}{3}(F-1)^{3/2}+\Psi F^n \quad \text{for} \quad F\geqq 1, \tag{5}$$

$$\Psi=\int_{(F-1)^{1/2}}^{L/a}(1+k^2)^{1-n}dk, \tag{6}$$

where L and a denote the cell half length and the Rayleigh range, respectively. Finally, q is obtained from F according to (1a) or (1b) for given Φ. The previously determined value (0.0148 cm^2) was used for the effective spot size (πr_f^2).

3. Results and Discussion

In order to investigate the dependences of Φ_c and n on operating pressure, irradiation wavelength and temperature, the experimental conditions must be carefully chosen since there are regions, where experiments are not possible due to either the non-selective process or gas breakdown.

The measurement of b_H (the specific dissociation rate of CHF_3) is further limited. The non-selective process or gas breakdown tends to occur at relatively low-pressure as the irradiation wavenumber and/or the gas temperature are increased. On the contrary, irradiation at lower wavenumber and/or at lower temperature tends to suppress the dissociation of CHF_3 drastically and the measurement of b_H becomes increasingly difficult.

3.1. Fluence Dependence of CTF_3 *Dissociation*

The Effect of Temperature

The q_T vs. Φ plot after deconvolution for the mixture of 1-µTorr CTF_3 and 5-Torr CHF_3 is shown in Fig. 1 for three temperatures levels: +25 °C (Curve *c*), −47 °C (Curve *b*), and −78 °C (Curve *a*). The laser line chosen was 9*R*(14) at 1075 cm^{-1}. The values for Φ_{cT} and n_T are found almost unaffected by a temperature change from 25° to −78 °C, as shown in Table 1.

Table 1. Values of Φ_{cT} and n_T

	CHF_3 pressure [Torr]	Line	Wave-number [cm^{-1}]	Temperature [°C]	Φ_{cT} [J/cm^2]	n_T
a	5	9*R*(14)	1075	−78	115	2.8
b	5	9*R*(14)	1075	−47	138	2.6
c[a]	5	9*R*(14)	1075	+25	136	2.5
d	85	9*R*(14)	1075	−78	76	4.9
e	85	9*P*(8)	1057	−78	62	5.8
f	45	9*R*(14)	1075	−78	79	3.4
g[a]	45	9*R*(14)	1075	+25	47	5.4
h[a]	35	9*R*(14)	1075	+25	60	4.2
i[a]	25	9*R*(14)	1075	+25	65	4.4
j[a]	15	9*R*(14)	1075	+25	110	2.6
k[a]	5 + 20 Torr Ar	9*R*(14)	1075	+25	65	3.3
l[a]	5 + 60 Torr Ar	9*R*(14)	1075	+25	39	4.2
m[a]	5 + 100 Torr Ar	9*R*(14)	1075	+25	34	4.8

[a] Our preceding work [9]

Table 2. Values of n_H/n_T

	CHF_3 pressure [Torr]	Line	Wave-number [cm^{-1}]	Temperature [°C]	n_T	n_H/n_T
d	85	9*R*(14)	1075	−78	4.9	1.23
j[a]	15	9*R*(14)	1075	25	2.6	1.15
c[a]	5	9*R*(14)	1075	25	2.5	1.12
m[a]	5 + 100 Torr Ar	9*R*(14)	1075	25	4.8	1.27

[a] Our preceding work [9]. The cases when the CHF_3 pressure was above 15 Torr at 25 °C were excluded because the reaction mechanism of CHF_3 is changed

The Effect of CHF_3 Pressure

The effect of CHF_3 pressure on the dissociation of CTF_3 is shown both in Fig. 1 and Table 1. The gas temperature was fixed at −78 °C and the irradiation line at 9*R*(14) (1075 cm^{-1}), while the CHF_3 pressure was chosen at 5 Torr (Curve *a*), 45 Torr (Curve *f*) or 85 Torr (Curve *d*).

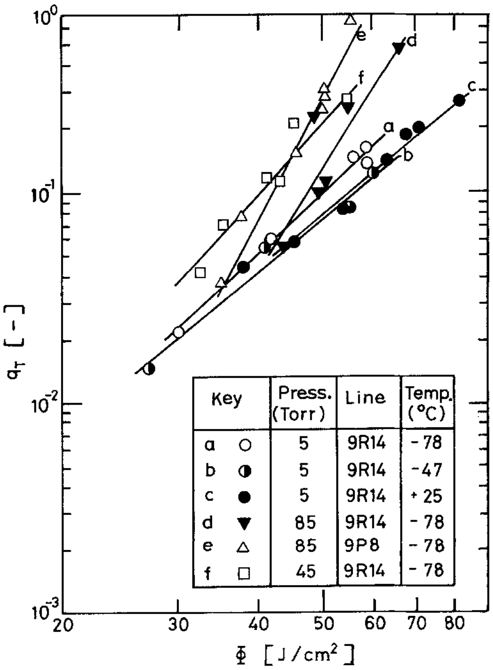

Fig. 1. Fractional conversion per pulse q_T for CTF_3 vs. fluence Φ

The value of n_T increases and that of Φ_{cT} decreases with increasing CHF_3 pressure. Also shown in Table 2 is the CHF_3 or buffer gas pressure dependence of n_T at the room-temperature, as reported in [9], which exhibits the same trend.

The Effect of Irradiation Wavelength

Results of the relation between q_T and Φ at *R*(14) line (1075 cm^{-1}) and *P*(8) line (1057 cm^{-1}) are compared in Fig. 1 for 85-Torr CHF_3 at −78 °C (Curve *d* vs. Curve *e*). Table 1 summarizes the values of n and Φ_{cT}. The variation of the irradiation laser line from 9*R*(14) at 1075 cm^{-1} to 9*P*(8) at 1057 cm^{-1} does not change n_T significantly.

All the data in Table 1 show strong correlation between n_T and CHF_3 pressure, and negligible dependences of n_T on temperature and irradiation wavelength in the region studied.

At first, the relation between Φ_{cT} and CHF_3 pressure will be discussed. The decrease of Φ_{cT} with increasing CHF_3 pressure is a characteristic behavior of the small molecules observed in CHF_2Cl [12], CF_3I [13], CF_3Cl [14], CDF_3 [15], etc. This phenomenon is considered due to collisional rotational hole filling that increases the average number of photons absorbed by one molecule at a given laser fluence. For the 9P(8) line (1057 cm^{-1}) irradiation at −78 °C, the trend is observed to continue until CHF_3 pressure reaches 100 Torr, while further increase in CHF_3 pressure reverses the trend due to collisional quenching.

Compared with a monotonous decrease of the specific dissociation rate at constant pulse energy (or equally monotonous increase in Φ_{cT} with pressure) in the 10–20 Torr range for larger molecules as pentafluoroethane-T [16] (CF_3CTF_2), trifluoromethane-T (CTF_3) was found to give a maximum dissociation rate at relatively high operating pressure.

Since operation at high-pressures is necessry in realistic laser isotope separation processes [17], it is advantageous for CTF_3 that the minimum Φ_{cT} is obtained at high-pressure using CO_2 lasers with standard pulse duration (100 ns – 1 µs). For an improvement of the characteristic curve of Φ_{cT} vs. operating pressure of halogenated ethanes such as CF_3CTF_2, the use of a short-pulse CO_2 laser may be required.

Secondly, the regular trend of increasing the value of n_T with CHF_3 pressure (or buffer gas pressure in our preceding study [9]) should be noted in Table 1. It may reflect an intrinsic effect of molecular collisions to multiphoton dissociation. For a qualitative explanation of the increasing trend of n with pressure, it will be necessary to solve numerically master equations of multiphoton dissociation with collisional terms included.

3.2. *Fluence Dependence of* CHF_3 *Dissociation*

As mentioned in Sect. 3.1, the condition where both b_T and b_H can be measured is limited. Figure 2 shows the plot of q_T and q_H as a function of Φ for 5-Torr CHF_3 at 25 °C and for 85-Torr CHF_3 at −78 °C. These two conditions were chosen as the cases, where the comparison of n_T and n_H is possible. Direct comparison of the values of the selectivity for the two cases is meaningless due to the following reason.

In the former case, the selectivity is constant (~50) until the CHF_3 pressure reaches 15 Torr but it decreases rapidly above 15 Torr for the irradiation at 9R(14) line (1075 cm^{-1}) at 25 °C. Namely, the former condition is at the plateau of the characteristic curve of the selectivity vs. pressure.

On the other hand, the latter condition [CHF_3 pressure 85 Torr, −78 °C, 9R(14) line at 1075 cm^{-1}] is in the region, where the selectivity starts to fall off with increasing pressure. The selectivity value at the plateau, if it exists, cannot be accurately determined in the latter case since it must be higher than 10^3.

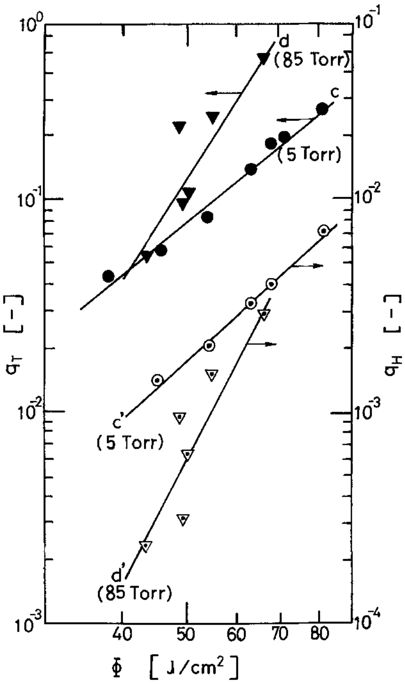

Fig. 2. q_T and q_H vs. Φ for 5 Torr CHF_3 at 25 °C and for 85 Torr CHF_3 at −78 °C

Instead of a direct comparison of the values of selectivity, a comparison of the values of n_T and n_H may be quite suggestive. As shown in Table 2, the ratio n_H/n_T is between 1.1 and 1.3 for all the cases studied including the previously mentioned cases at the room-temperature [9], although the value of n_T varies from 2.5 to 4.9 depending on the CHF_3 or Ar pressure.

The near agreement of the values of n_T and n_H may be due to the selectivity-determining mechanisms: CHF_3 dissociation is originated from its multiphoton process rather than the energy transfer from CTF_3. The dissociation of CHF_3 parallels the dissociation of CTF_3 and they only differ in the linear absorption cross-section.

Based on (1a), the selectivity in the region where the reaction saturation does not occur is expressed as

$$S_0 \equiv q_T/q_H = \Phi_{cT}^{-n_T} \cdot \Phi_{cH}^{n_H} \cdot \Phi^{n_T - n_H}\,. \tag{7}$$

Since n_T and n_H are close, S_0 does not dependent much on Φ, as shown by (7) and in Fig. 3.

If the geometrically biased selectivity in this region is defined by $S \equiv b_T/b_H$, the error, when S is used instead of S_0, is estimated as

$$\zeta = S/S_0 = \frac{\int_0^{L/a} (1+k^2)^{1-n_T} dk}{\int_0^{L/a} (1+k^2)^{1-n_H} dk}\,. \tag{8}$$

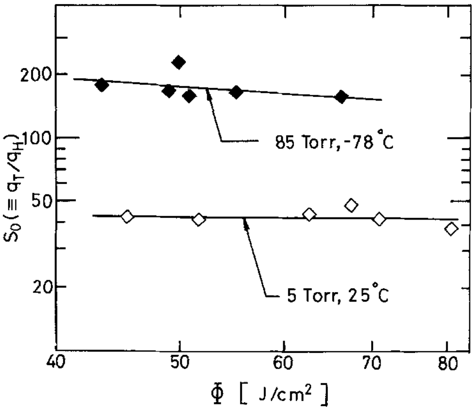

Fig. 3. Intrinsic selectivity S_0 vs. Φ for the same conditions as in Fig. 2

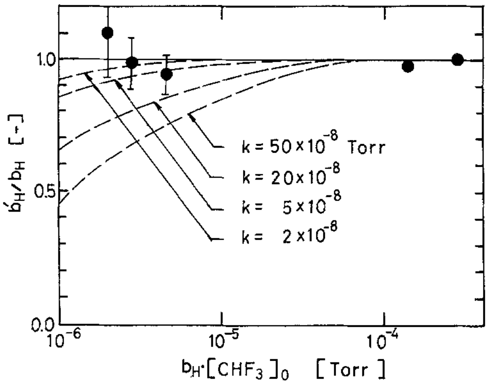

Fig. 4. b'_H/b_H vs. $b_H[CHF_3]_0$ plot to determine maximum value of k

Since ζ in (8) does not deviate from unity significantly when $n_T \simeq n_H$, S is alternatively used for the discussion of the selectivity in the next section instead of S_0 which requires extensive data collection for n_H and n_T.

By shifting the irradiation wavenumber from 1075 cm^{-1} [9R(14) line] to 1057 cm^{-1} [9P(8) line], the selectivity was further increased.

The value of b_H became too small to be determined accurately when the selectivity exceeds 10^3 in the depletion measurement of CHF_3 after irradiation.

As will be discussed next, the measurement of the selectivity at 1057 cm^{-1} at -78 °C was attempted using a C_2F_4 analysis. Tuccio and Hartford [18] proposed a method to determine the selectivity in H–D separation on the basis of the following assumptions. Tetrafluoroethylene C_2F_4 is formed in the dissociation reaction $CHF_3 \rightarrow CF_2 + HF$ followed by the reaction $2CF_2 \rightarrow C_2F_4$. The CF_2 radical may not result in C_2F_4 due to secondary reactions (possibly wall reactions, reaction with oxygen leaked in the cell, etc.).

The application of this method to tritium isotope separation is simpler and straightforward compared with that of deuterium isotope separation, since the partial pressure of resonant CTF_3 is more than 10^6 times smaller than that of CHF_3, and CF_2 radical formation originated from CTF_3 dissociation is negligible. When a CF_2 radical is assumed to be lost in the first-order way before recombination, the disappearing rate of CF_2 radicals can be written as a function of time θ after primary dissociation by

$$\frac{d[CF_2]}{d\theta} = -k_1[CF_2]^2 - k_2[CF_2], \tag{9}$$

where k_1 and k_2 are the rate constants for recombination and the secondary reaction.

The rate of C_2F_4 formation is given by

$$\frac{d[C_2F_4]}{d\theta} = k_1[CF_2]^2. \tag{10}$$

Let the apparent specific dissociation rate b'_H be defined by $b'_H = -\ln(1-X_H)/t$ with $X_H = 2[C_2F_4]_\infty/[CHF_3]_0$, where $[CHF_3]_0$ is the CHF_3 pressure before irradiation and $[C_2F_4]_\infty$ is the C_2F_4 pressure after the termination of the radical reaction. The value for b'_H is always less than or equal to that of b_H. Since almost all C_2F_4 molecules are originated from the dissociation of CHF_3 but not CTF_3, the relation between b'_H and b_H is given by

$$b'_H = b_H\eta \equiv b_H\left(1 - \frac{\ln(1+z)}{z}\right), \tag{11}$$

where η is the efficiency of the radical recovery as C_2F_4, and the dimensionless parameter z is given by

$$z = b_H[CHF_3]_0/k \quad \text{with} \quad k = k_2/k_1. \tag{12}$$

The larger the value of z is, the closer to unity becomes the value of η. Consequently, the b_H value can be calculated from experimentally obtained b'_H and k even if b_H cannot be determined by depletion measurement.

In order to determine the value of k, a series of experiments were performed under the condition where both b'_H and b_H can be measured simultaneously. The sample gas (CHF_3: 5 Torr, CTF_3: 1 µTorr) was irradiated at 9R(14) line (1075 cm^{-1}) and -47 °C.

Figure 4 shows experimentally obtained b'_H/b_H as a function of $b_H\,[CHF_3]_0$. The broken lines are theoretical curves with k values assumed as given in the figure. No deviation of b'_H/b_H from unity was observed even at the lowest value of $b_H[CHF_3]_0$.

The estimation of the experimental error involved indicates that k is not larger than 4×10^{-8} Torr. For H–D separation at room-temperature, k was estimated to be 5.5×10^{-8} Torr by Tuccio and Hartford and to be less than this value by Marling et al. [6].

The selectivity for 85-Torr CHF_3 at -78 °C with irradiation at 9R(14) line (1075 cm^{-1}) is found to be

Table 3. The selectivity vs. operating pressure at 1 μTorr CTF_3 pressure

	CHF_3 pressure	$b_T \times 10^6$	$b'_H \times 10^6$	$b_H \times 10^6$	$S = b_T/b_H$
(I)	85 Torr	64.9	$< 3.2 \times 10^{-3}$	$< 4.3 \times 10^{-3}$	$> 15{,}000$
(II)	165 Torr	18.0	$< 1.1 \times 10^{-3}$	$< 1.6 \times 10^{-3}$	$> 11{,}000$
(III)	205 Torr	21.1	$< 0.83 \times 10^{-3}$	$< 1.2 \times 10^{-3}$	$> 18{,}000$

Laser line: $9P(8)$ at 1057 cm^{-1}
Temperature: −78 °C
Pulse energy E_0: 0.8 J

between 160 and 200 for the fluence range of 40–70 J/cm^2. The selectivity on the lower wavenumber side is much larger than these values. But accurate determination becomes increasingly difficult. The tetrafluorethylene concentration became below the detection limit at $9P(8)$ line irradiation at 1057 cm^{-1} even at such a high CHF_3 pressure as 205 Torr, and there was no way to investigate the selectivity vs. operating pressure characteristics at this condition. Consequently, only the minimum value of the selectivity at a certain CHF_3 pressure levels will be discussed assuming k is equal to the maximum possible value (4×10^{-8} Torr).

Table 3 summarizes the experimental results: the selectivity is at least larger than 10^4 for 85, 165, and 205 Torr. The variation of the minimum value of the selectivity in Table 3 with CHF_3 pressure is due to the different irradiation pulse number (10^5 for 85 Torr CHF_3, and 2×10^5 for 165 and 205 Torr CHF_3), different values of b_T and different amount of gas injected into the radio gas chromatograph. This variation does not imply any trend in the selectivity vs. operating pressure characteristics.

3.3. MPD *Spectra*

MPD Spectrum of CTF_3

Figure 5 indicates the effects of temperature and gas pressure on the MPD spectrum (q_T vs. irradiation wavenumber for fixed Φ). The fluence is normalized to 54 J/cm^2.

For all the cases shown in Fig. 5, the value of q_T at $9P(10)$ line (1072 cm^{-1}) is higher than that at $9P(8)$ line (1057 cm^{-1}). This naturally leads to the conclusion that the peak of the multiphoton dissociation spectra of CTF_3 lies between these wavenumbers but closer to 1072 cm^{-1}. The peak is probably located in the region of 1065–1070 cm^{-1}, where the CO_2 laser lines are unavailable or very weak, but not in the neighbourhood of 1057 cm^{-1}, as suggested by Nève de Mévergine et al. [19].

The dependence of the specific dissociation rate b on the pulse energy varies from the n^{th} power dependence in (3) to the 3/2-power dependence in the high-E_0 region.

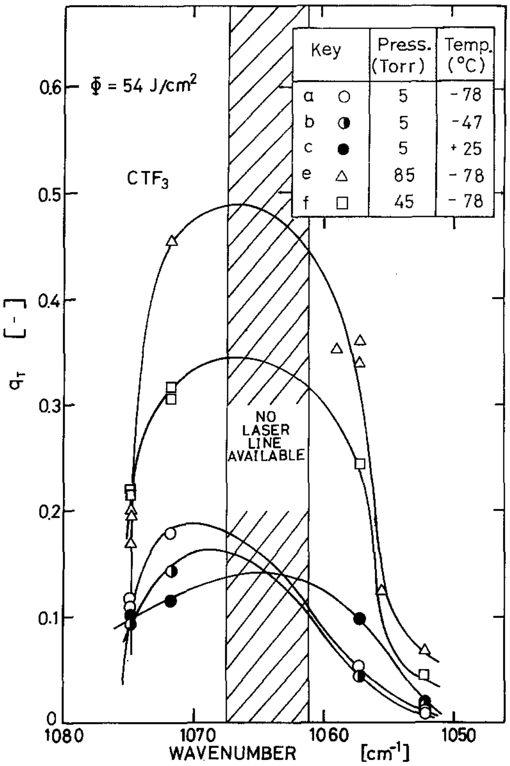

Fig. 5. MPD spectra of CTF_3: q_T vs. irradiadiation wavenumber at $\Phi = 54\ J/cm^2$

Normalization of the pulse energy with 3/2-power dependence must be limited to the tightly focused geometry ($F \gg 1$). For other cases ($F \sim 1$ or $F < 1$), (1a) should be used with accurate values of Φ_{cT} and n. Application of the 3/2-power dependence may lead to erroneous spectra when the focal fluence is not much greater than the critical fluence.

The effect of the gas temperature was investigated at a fixed pressure of 5 Torr for three temperature levels: 25 °C (Curve *c*), −47 °C (Curve *b*), and −78 °C (Curve *a*).

The spectrum for 5 Torr CHF_3 at 25 °C (Curve *c*) is relatively flat and q_T values at such wavenumber as 1075 cm^{-1} [$9R(14)$ line], 1072 cm^{-1} [$9R(10)$ line], and 1057 cm^{-1} [$9P(8)$ line] do not differ considerably.

If this were the only result obtained, it would be possible to assume that the peak is either at 1075 cm^{-1}, 1072 cm^{-1} or 1057 cm^{-1}. But the comparison of Curves *c*, *b*, and *a* yields a much closer view of the spectra.

The multiphoton spectra are expected to be sharpened by reducing the gas temperature as well as the linear absorption spectra. As a result, in the neighbourhood of the MPD peak, q_T will be increased with reduced temperature.

Such increase was observed at 1072 cm^{-1} [9R(10) line], but the trend was reversed at 1057 cm^{-1} [9P(8) line]. This indicates that the line at 1072 cm^{-1} is within the two inflection points of the spectra while the line at 1057 cm^{-1} is not. This also confirms our estimation of the location of the MPD peak at 1065–1070 cm^{-1}.

As the next step, Curves a, e, and f in Fig. 5 are compared to see the effect of CHF_3 pressure on q_T at −78 °C. More than a four-fold increase of q_T is observed at 1072 cm^{-1} [9R(10) line] and at 1057 cm^{-1} [9P(8) line] when the CHF_3 pressure is increased from 5 to 85 Torr. This is due to the collision-assisted rotational hole-filling, as discussed in Sect. 3.1 and shown in Table 1.

3.4. MPD *Spectra of* CHF_3

The temperature dependence of the MPD spectra of CHF_3 was obtained only for 5-Torr CHF_3, as shown in Fig. 6. No attempt was made to investigate the CHF_3 pressure dependence on the MPD spectra, because the increase of CHF_3 pressure in the high wavenumber range tends to evoke the isotopically non-selective process or gas breakdown. The irradiation wavenumber was shifted to the high wavenumber side until accurate measurement of b_H became possible.

As discussed previously, the dissociation of CHF_3 follows the multiphoton absorption of CHF_3 [9]. Since the irradiation wavenumber is far from the band center of the corresponding linear absorption of CHF_3 near 1140 cm^{-1}, the temperature reduction functions to decrease q_H. The very sharp increase of q_H of the curves in Fig. 6 toward the high wavenumber side may be attributed to the initiation of the isotopically non-selective process discussed in [9].

Figure 6 shows that the temperature reduction from 25° to −47 °C is more effective than that from −47° to −78 °C: the curves for −78° and −47 °C are close compared with the curve for 25 °C. This fact may support our explanation for the mechanism deteriorating the selectivity at high-pressure: absorption by molecules at hot bands excited during the duration of a laser pulse by a collisional process. Once hot-band absorption is suppressed at −47 °C, further decrease of temperature to −78 °C does not affect the MPD spectrum significantly.

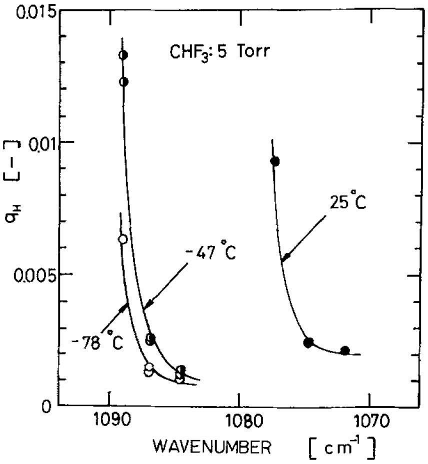

Fig. 6. MPD spectra of CHF_3: q_H vs. irradiation wavenumber at $\Phi = 54\,J/cm^2$

4. Conclusion

Multiphoton dissociation of the CTF_3/CHF_3 system was investigated in relation to tritium isotope separation by CO_2 laser irradiation.

A deconvolution model where the fractional conversion per pulse q is expressed as $q = (\Phi/\Phi_c)^n$ was utilized, and the effects of CHF_3 pressure, irradiation wavelength and gas temperature to the yield and the selectivity were tabulated in terms of the values of n and Φ_c. Observed results are as follows.

1) The values of n is unaffected by the change of the temperature and irradiation wavenumber but it increases significantly with increasing CHF_3 pressure.

2) The value of Φ_{cT} decreases with increasing CHF_3 pressure up to 85 Torr.

3) The value of n_H is always slightly greater than that of corresponding n_T.

4) The selectivity exceeds 10^4 at 9P(8) line (1057 cm^{-1}) at −78 °C.

5) The study of the multiphoton spectra of CTF_3 based on the deconvolution model shows that the peak is located at 1065–1070 cm^{-1}.

6) The study of the MPD spectra of CHF_3 gives the supporting evidence to the mechanism that deteriorates selectivity.

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