

# Selectivity Enhancement in Tritium Isotope Separation by Multiple Frequency Multiple Photon Dissociation of the CTF<sub>3</sub>/CHF<sub>3</sub> System

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**Abstract.** Isotope separation of tritium by multiple photon dissociation process in multiple frequency fields of a TEA-CO<sub>2</sub> laser is reported for the first time. A ten-fold improvement in the bulk selectivity was obtained in 8.5 Torr CTF<sub>3</sub>/CHF<sub>3</sub> in the presence of buffer gas at room temperature using 9R(8) to 9R(14) CO<sub>2</sub> laser lines compared to single frequency excitation. Investigations of various process parameters such as exciting laser frequencies, pulse energy, sample and buffer gas pressure indicate that this is a promising technique for the separation of tritium.

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Extensive studies in Infrared Multiphoton Dissociation (IRMPD) have indicated a tremendous potential of this technique in laser isotope separation (LIS) [1]. For lighter elements like hydrogen, carbon, etc., where large isotope shifts exist in the vibrational spectrum, good separation factors have been reported [2]. Interest in developing technologies for removing tritium from light water or from heavy water reactors has necessitated the separation of this radioactive isotope by LIS.

Due to the lack of a tunable and efficient laser in the frequency region of the absorption of water, tritium from contaminated water is first transferred to an appropriate organic phase in the presence of a catalyst. It is then removed from the organic phase by isotope selective MPD and the cycle can be repeated. Trifluoromethane-T (CTF<sub>3</sub>) is the most extensively studied molecule for tritium isotope separation using the pulsed CO<sub>2</sub> laser [3–8]. However, in order to decrease the MPD critical fluence for achieving a larger processing rate and also the efficiency of the initial isotope exchange process, various other molecules have been tried with due consideration of their spectroscopic properties and the rate of tritium ex-

change [9–14]. Most of the studies on tritium separation were carried out at a single exciting frequency, where high fluences were required in order to overcome the dissociation threshold of the desired species. Nevertheless, at higher intensities, due to power broadening, dissociation of the off-tuned undesired species becomes significant resulting in a decrease of the selectivity.

Kato et al. [14] have summarized and compared the behaviour of various T/H separation systems under such tightly focused conditions. However, selectivity can be improved by various techniques such as buffer gas addition [4], optimization of irradiation geometry [7] and lowering the temperature of the sample. Under favourable conditions, a high intrinsic selectivity exceeding 10<sup>4</sup> has been observed in a moderately high pressure system at –78 °C [8].

But in a more elegant and efficient way, using multiple frequency IR-laser fields, one can in principle excite and dissociate those molecules whose MPD in a single frequency field requires very high fluence. CTF<sub>3</sub>, a small-sized molecule, has a vast ladder of discrete vibrational states and its vibrational quasi-continuum (QC) onset is located at a relatively high energy. In

such a case, multistep resonant excitation using multiple frequency laser fields makes it possible to overcome the discrete vibrational levels in relatively weak IR-laser fields and thus improve the selectivity and yield of MPD. By using two-colour excitation, such improvements in the selectivity have been reported for many isotopes such as deuterium [15, 16], tritium [11], sulphur [17], carbon [18], etc.

In the present work, we have obtained multiple frequencies from a single pulsed  $\text{CO}_2$  laser using a simple approach. By employing this laser, we have carried out the MPD of  $\text{CTF}_3$  in the presence of  $\text{CHF}_3$  under multiple-frequency fields. By comparing these results with single-frequency experiments, we report for the first time an increase in selectivity of tritium separation with multiple frequency excitation in the  $\text{CHF}_3/\text{CTF}_3$  system. Although we have not optimized the conditions for obtaining high selectivity, investigations were carried out at various exciting laser wavelengths, pulse energy and sample/buffer gas pressure for gaining an insight into each effect.

## 1. Experimental

Trifluoromethane-T ( $\text{CTF}_3$ ) was prepared by hydrogen isotope exchange of  $\text{CHF}_3$  (Matheson, 99% purity) with tritiated water in the presence of dimethyl sulfoxide and sodium hydroxide by a method similar to that reported in [3]. Typically the  $\text{CHF}_3$  sample used in our experiments had 0.2 ppm of  $\text{CTF}_3$ .

A commercial laser (Lumonics model TEA 103-2) was used for irradiation experiments. The 2.2 m long cavity of the laser (discharge cross-section  $9\text{ cm}^2$ ) was formed with a Littrow mounted blazed grating and a Ge output mirror ( $R=10\text{ m}$ ). The principle of operation of the laser on multi line is shown in Fig. 1 and is discussed in detail elsewhere [19]. It will be described here only briefly. Even when the grating is tuned to resonate for a particular rotational line, the resonance condition may also hold for a few neighbouring rotational lines as well provided the output mirror has a concave geometry. Low gain lines, owing to their smaller population inversion, saturate at a slower rate, thus resulting in an overall reduction in competition

among themselves. Hence even with a partial spatial overlap, a group of neighbouring low gain lines may simultaneously grow to give multiple frequency output. In this case there is no need for any spatial control which is otherwise achievable by a rather difficult and inefficient aperture technique. Therefore, by an appropriate tuning of the grating angle to satisfy the resonance condition, different sets of lines can be made to lase simultaneously. The pulse energy was measured by a pyroelectric joule meter (Lumonics 20D). The shot-to-shot variation in pulse energies was within  $\pm 5\%$ . The laser frequencies were measured by a spectrum analyzer (Optical Engineering Inc.).

All irradiations were carried out at room temperature in a pyrex cell (30 cm in length and 3.5 cm in diameter) equipped with polished KCl windows and a greaseless stopcock. Focusing of the laser beam was done at the centre of the cell by a  $\text{BaF}_2$  lens ( $f=25\text{ cm}$ ). Excitation in the  $\nu_2$  absorption band of  $\text{CTF}_3$  in the pressure range 2–8.5 Torr of  $\text{CHF}_3$  were carried out using different rotational lines in the R branch of the  $9.6\text{ }\mu\text{m}$  band of the  $\text{CO}_2$  laser. Various fluence conditions were obtained by attenuating the laser beam with polyethylene films of different thickness. All single frequency irradiations were carried out using a nitrogen-free laser gas mixture to avoid the long tail ( $\approx 1\text{ }\mu\text{s}$ ) after the initial laser pulse (100 ns FWHM). However, addition of a small amount of nitrogen was found to be efficient for obtaining better pulse energy in case of multiple frequency emission. Using a photon drag detector (Rofin), the temporal profiles of the laser pulses in both cases were found to be similar.

Irradiated samples were cryogenically transferred to a radio-gas chromatograph (GC) for analysis. The radio-GC consisted of a commercial Shimadzu GC-R1A equipped with thermal conductivity detector (TCD) and an indigenously built proportional counter (10 ml, 3 kV) for the analysis of tritium bearing species. A Porapak Q column (80–100 mesh, 2 mm i.d., 5 m long) was used at  $35^\circ\text{C}$  with He carrier gas (flow rate 25 ml/min) to separate the only photoproduct  $\text{C}_2\text{F}_4$  from the starting mixture of  $\text{CHF}_3/\text{CTF}_3$ . Before entering the counter, the sample and the carrier gas were mixed with methane (40 ml/min) in order to

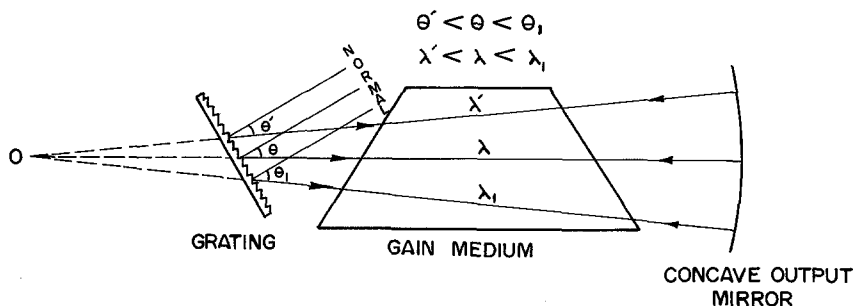


Fig. 1. Schematic of multiple frequency generation in a TEA- $\text{CO}_2$  laser. Due to the concave geometry of the output mirror, the resonance condition is satisfied simultaneously for a number of frequencies

suppress some spurious signals in the counter. The counter was first calibrated and an excellent linearity was observed between the number of counts and the amount of active tritiated sample injected in the GC. Thus depletion in  $\text{CTF}_3$  and  $\text{CHF}_3$  could be independently and simultaneously measured by the counter and the TCD respectively. The determinations of  $\text{CHF}_3$  and  $\text{CTF}_3$  were reproducible to within  $\pm 1\%$ . The  $\text{C}_2\text{F}_4$  peak was also used to counter-check the  $\text{CHF}_3$  dissociation.

## 2. Results

### 2.1. Single Frequency Excitation

The frequency dependence of  $\text{CTF}_3$  MPD was determined at discrete frequencies of the  $\text{CO}_2$  laser [from  $9R(8)$  to  $9R(26)$ ] in the  $\nu_2$  absorption profile. The cell-averaged dissociation probabilities per pulse  $d_T$ ,  $d_H$  and the selectivity were measured using various pulse energies and sample pressures. Under focused geometry of excitation  $d_T$  and  $d_H$  were found to have  $3/2$  and  $2$  power dependence on pulse energy  $E$ . Therefore with increasing  $E$ , the process selectivity  $S_{T/H}$  was found to decrease. Both  $d_T$  and  $d_H$  increased with increase in sample pressure, while  $d_H$  increased more rapidly than  $d_T$  resulting in lower selectivity. The increase in  $d_T$  of the resonant species  $\text{CTF}_3$  with increasing pressure is due to the collisional relaxation of the rotational bottleneck. Since the collision frequency of  $\text{CHF}_3$  with another  $\text{CHF}_3$  is about  $10^6$  times greater than with  $\text{CTF}_3$ , it is reasonable that  $d_H$  will have strong pressure dependence and its increase can be explained in terms of collision-induced dissociation of pre-excited  $\text{CHF}_3$ .

Using the  $1\ \mu\text{s}$  long laser pulse by adding  $\text{N}_2$  in the laser gas mixture, the selectivity was found to be poorer than the  $100\ \text{ns}$  laser pulse excitation for the same pulse energy. The decrease in  $d_T$  may be caused by the lower peak intensity and/or by the increased collisional deactivation of  $\text{CTF}_3^*$  while  $d_H$  is increased due to the collision-induced dissociation of pre-excited  $\text{CHF}_3$  during the longer pulse duration.

Figure 2 shows the MPD spectra of  $\text{CTF}_3$  and  $\text{CHF}_3$  using single colour irradiation ( $1\ \text{J}$  pulse energy) of  $8.5\ \text{Torr}$   $\text{CHF}_3$  containing  $0.2\ \text{ppm}$  of  $\text{CTF}_3$ . With the present laser set up and irradiation geometry the focal fluence was estimated to be  $\approx 175\ \text{J cm}^{-2}$ . In the frequency range studied here,  $d_T$ ,  $d_H$  and  $S_{T/H}$  (Fig. 2) are in excellent agreement with the results of earlier investigations on the IRMPD of  $\text{CHF}_3/\text{CTF}_3$  system [4–6]. A peak for  $d_T$  was observed near  $1074\ \text{cm}^{-1}$ . The increase in  $d_H$  for excitation at higher frequency ( $\text{CTF}_3$   $Q$ -branch:  $1077\ \text{cm}^{-1}$ ) can be attributed to the increasing absorption tails of either the  $\nu_2$  band of  $13\text{-CHF}_3$  ( $Q$ -branch:  $1116\ \text{cm}^{-1}$ ) and/or the  $\nu_2$  band of  $12\text{-CHF}_3$

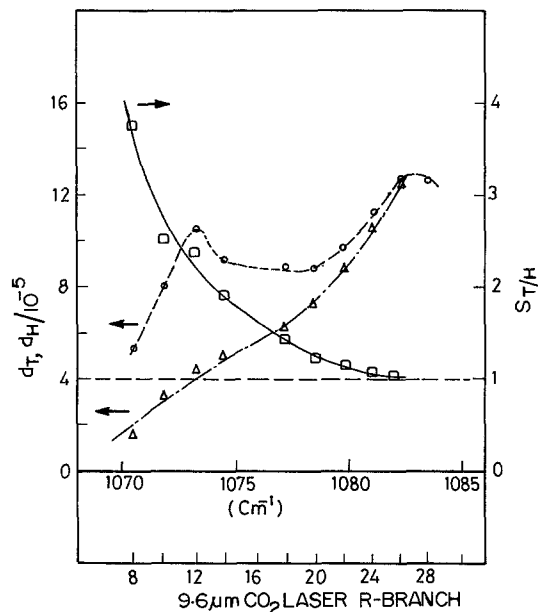


Fig. 2. Frequency dependence of the cell-averaged dissociation probability per pulse,  $d_T(\circ)$  and  $d_H(\triangle)$  under single frequency excitation. The right-hand ordinate plots the single step selectivity factor defined as  $S_{T/H}(\square) = d_T/d_H$ . Sample:  $8.5\ \text{Torr}$   $\text{CHF}_3$  containing  $0.2\ \text{ppm}$  of  $\text{CTF}_3$  at room temperature; pulse energy:  $1\ \text{J}$

( $1141\ \text{cm}^{-1}$ ). As mentioned earlier, the isotopic selectivity and yield can be improved by optimizing various experimental parameters like irradiation geometry, gas temperature, addition of buffer gas, etc. However, the primary aim of our present investigation was to study the effect of multiple frequency excitation on the selectivity and yield of MPD compared to usual single frequency excitation. Therefore, further experiments were carried out in this direction.

### 2.2. Multiple Frequency Excitation

Table 1 shows the effect of multiple frequency excitation on the selectivity. Two groups of lines  $9R(20)$  to  $9R(26)$  near the peak and  $9R(8)$  to  $9R(14)$  in the red wing of the  $Q$ -branch of  $\text{CTF}_3$  were chosen for irradiation. As can be seen from the table, in both cases selectivity improved by a factor of 4 with multiple frequency excitation (compare run 5 with run 1, and run 11 with run 7). The comparison of these results was done under the same sample pressure and the fluence conditions. In the later case, the total pulse energy of  $1\ \text{J}$  is distributed over the four frequencies. It should be mentioned that although the total working laser fluence under focused conditions meets the criterion of the critical fluence for dissociation of  $\text{CTF}_3$  ( $\approx 65\ \text{J cm}^{-2}$ ), the fluence on each individual line will fall short of this requirement. Therefore, single frequency experiments using the same energies of the

**Table 1.** Frequency dependence of  $d_T$ ,  $d_H$ , and  $S_{T/H}$  in the IRMPD of 8.5 Torr  $\text{CHF}_3$  containing 0.2 ppm  $\text{CTF}_3$  under single and multiple frequency excitation with a total pulse energy of 1 J

Run no.	Frequency [ $\text{cm}^{-1}$ ]	$d_H \times 10^5$ $d_T \times 10^5$		$S_{T/H}$
		(per pulse)		
1	9R(8)	1.44	5.38	3.74
2	1070.5	3.20	8.00	2.50
	9R(10)			
3	1071.9	4.40	10.60	2.41
	9R(12)			
4	1073.3	5.00	9.10	1.82
	9R(14)			
5	1074.6	0.34	4.73	13.91
6	9R(8)–9R(14)	6.20	8.90	1.44
	9R(18)			
7	1077.3	7.16	8.86	1.24
	9R(20)			
8	1078.6	8.60	9.80	1.14
	9R(22)			
9	1079.8	10.60	11.20	1.06
	9R(24)			
10	1081.1	12.68	12.80	1.01
	9R(26)			
11	1082.3	0.38	1.98	5.21
	9R(20)–9R(26)			

individual lines as obtained in the multiline emission could not be carried out.

The effect of argon buffer gas on the selectivity and yield of MPD in single and multiple frequency excitation were studied. For these studies the sample and the Ar pressures were kept at 8.5 and 20 Torr respectively. The results are shown in Table 2. In general, at a given pressure of the absorbing species, the inert gas initially increases the MPD rate due to collisional relaxation of rotational bottle neck particularly in small molecules having lower density of vibrational states. Then at higher pressure of the buffer gas  $V \rightarrow T$

relaxation dominates and the MPD rate decreases. The buffer gas pressure at which such inversion in the yield occurs is also a function of the excitation frequency [15]. Probably for this reason, in the present experiment where the Ar pressure was kept constant at 20 Torr,  $d_T$  behaves differently with excitation by R(8) and R(12) lines. On the other hand, the MPD yield for non-resonating species  $d_H$  should decrease due to the collisional deactivation with buffer gas addition. But Makide et al. [4] reported an increase in  $d_H$  with Ar pressure above 10 Torr, which is probably due to collision-induced dissociation of pre-excited  $\text{CHF}_3$  molecules. However, in the present set of experiments, Ar modified  $d_H$  and  $d_T$  in such a fashion that it yielded higher process selectivity in all cases.

### 3. Discussion

The selectivity ( $S_{T/H}$ ) achieved in the present work under tightly focused geometry can be used for a rough estimation of the geometrically unbiased intrinsic selectivity ( $S_{T/H}^0$ ) for comparison with other work reported in the literature. However, one should note that the intrinsic selectivity is only estimated and should not be mixed up with the bulk selectivity which is an experimental quantity. Such a quantity is meaningful under conditions where the laser fluence matches the critical fluence for  $\text{CTF}_3$  yielding unit dissociation probability. Following the procedure of [10]:

$$S_{T/H}^0 = (S_{T/H})^{2n_H/3},$$

where  $n_H$  is the slope of the log-log plot of dissociation probability for  $\text{CHF}_3$  and laser fluence. Takeuchi et al. [7, 8] have carried out extensive determinations of  $n_H$  for different pressures and temperatures of  $\text{CHF}_3$ . Taking  $n_H$  values from their work to be 3 for 8.5 Torr  $\text{CHF}_3$  containing 0.2 ppm  $\text{CTF}_3$  and 4 in the presence of an additional 20 Torr Ar, the intrinsic selectivity was

**Table 2.** Comparison between the yields and selectivities in case of single and quadruple frequency MPD in the presence of argon

Laser line (w)/energy, E [J]				$P_{\text{Ar}}$ [Torr]	$d_H \times 10^5$	$d_T \times 10^5$	$S_{T/H}$	$S_{T/H}^0$
$w_1/E_1$	$w_2/E_2$	$w_3/E_3$	$w_4/E_4$					
9R(8)	–	–	–	–	1.44	5.38	3.74	13.9
1.0	–	–	–	20	3.60	14.57	4.05	41.7
–	–	9R(12)	–	–	4.40	10.60	2.41	5.8
–	–	1.0	–	20	3.43	9.09	2.65	13.5
9R(8)	R(10)	R(12)	R(14)	–	0.34	4.73	13.91	193.5
0.22	0.26	0.17	0.35	20	0.28	10.73	38.32	16690.5
9R(20)	R(22)	R(24)	R(26)	–	0.38	1.98	5.21	27.1
0.15	0.30	0.40	0.15	20	0.34	4.31	12.69	876.1

found to increase from 193 to more than  $10^4$  in the presence of 20 Torr Ar with quadruple frequency 9R(8) to 9R(14) excitation.

In the present investigation, we have studied important aspects of selectivity enhancement of MPD process. Let us consider the mechanism of this. The CTF<sub>3</sub>/CHF<sub>3</sub> system can be classified as a small-sized molecular system wherein the onset of QC of vibrational levels is located at a fairly high energy. The vibrational state density is  $\approx 10^5/\text{cm}^{-1}$  at  $10500\text{ cm}^{-1}$  (equivalent to the absorption of 10 CO<sub>2</sub> laser photons) which is an order of magnitude lower than for the SF<sub>6</sub> molecule. The MPD of such molecules in a single frequency laser field requires high fluence. From our experiments on two frequency MPD of CDF<sub>3</sub> [15], we expect a more efficient MPD process for CTF<sub>3</sub> under multiple frequency excitation since the anharmonicity of the pumped mode ( $X_{22} = -0.6\text{ cm}^{-1}$ ) is larger compared to  $X_{55} = -0.25\text{ cm}^{-1}$  of CDF<sub>3</sub> [22].

The dependence of multiple photon excitation and dissociation on both laser intensity and fluence have been predicted from theory [1]. Subsequently it was shown theoretically that a non-linear intensity dependence exists in the case of excitation/dissociation of small molecules [20]. It has also been demonstrated experimentally [21] that such dependence is more pronounced when the small molecule is excited at frequencies away from its absorption band. In the present case, the laser excitation frequency is closer to the resonance with  $\nu_2$  mode of CTF<sub>3</sub> and therefore the CHF<sub>3</sub> molecule is in a highly off-resonant condition. This fact and the observed behaviour of  $d_T$  and  $d_H$  with pulse energy and long pulse irradiation (cf. Sect. 2.1) suggest that the selectivity can be improved by working with lower intensity and fluence. However, in single frequency excitation a decrease in laser intensity by lowering the fluence is possible only within certain limits, because a definite threshold fluence is required to effect the transition through the QC.

Therefore, by changing over to multiple frequency excitation the selectivity of the MPD can be improved. Distributing the same total laser fluence over several frequencies will automatically lead to a reduction of intensities on each frequency for the individual excitation steps. In addition, one can in principle build up the selectivity by taking advantage of multiplication of the selectivities attained in the individual excitation steps [23]. From the data of Table 2, it can be seen that by distributing 1 J of energy of the 9R(8) line over four frequencies 9R(8) to 9R(14) an almost ten-fold improvement in selectivity was achieved in the presence of buffer gas. The results were similar for excitation by another group of lines namely 9R(20) to R(26). It has been demonstrated that by changing over to multiple frequency excitation, the dissociation yield can also be

improved by elimination of molecular "sticking" which is the major bottleneck for excitation through the discrete vibrational levels in the case of small molecules. The mechanism of such molecular "sticking" is discussed in detail by Evseev et al. [18] and multiple frequency excitation/dissociation for eliminating such "sticking" has been applied to the CF<sub>2</sub>HCl molecule in the context of 13-C isotope separation. Although we have not optimized the dissociation yield, this could be done by appropriately altering the relative energies on individual lines of the multiple frequency laser fields.

#### 4. Conclusions

In conclusion, we have demonstrated an efficient method for the dissociation of CTF<sub>3</sub> using multiple frequency IR-laser excitation. By adjusting various parameters like substrate and/or buffer gas pressure, laser frequency, pulse duration and relative fluences it will be possible to improve upon the present results. Finally, such multiple frequency excitation/dissociation of a molecular system can be very helpful for practical laser isotope separation in terms of the reduced threshold fluence requirement and optimum photon utilization.

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