T/D Isotope Selectivity in CO_2 Laser Induced Multiple-Frequency Multiphoton Dissociation of Trifluoromethane-T

A. K. Nayak, R. S. Karve, S. K. Sarkar, K. V. S. Rama Rao, and J. P. Mittal

Multi Disciplinary Research Section, Bhabha Atomic Research Centre, Trombay, Bombay-400085, India

Abstract. Isotope-selective multiphoton dissociation of CTF_3 in the presence of CDF_3 by TEA CO_2 laser is studied. The highest T/D selectivity of 58 was observed at a sample pressure of 2 Torr in the presence of 20 Torr of argon on excitation by the $9P(24)$ CO_2 laser line. The effect of multiple-frequency irradiation on selectivity is studied in the P and Q branches of the v_2 absorption band of CTF_3. No improvement in the selectivity is noticed on going from single- to multiple-frequency irradiation. These results are compared with previous multiple-frequency work on the CTF_3/CHF_3 system, and explained in terms of strong spectroscopic interference from $^{13}CDF_3$ in the present case.

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Extensive studies on infrared multiphoton dissociation (IRMPD) have indicated the potential of this technique for laser isotope separation (LIS) [1], especially for lighter elements like hydrogen and carbon [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 unavailability of tunable and efficient laser in the region of absorption of water, tritium from contaminated water is first transferred to an appropriate organic phase in the presence of a catalyst. Then tritium is removed from the organic phase by isotope-selective MPD and the cycle can be repeated. Trifluoromethane-T (CTF_3) is the most extensively studied molecule for tritium isotope separation using a pulsed CO_2 laser [3–8]. However, in order to improve the selectivity 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 exchange [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. However, selectivity can be improved by various techniques, for example buffer gas addition [4], optimization of irradiation geometry [7] and low temperature of the sample [8].

Using multiple frequency IR-laser fields, one can in principle excite and dissociate much more efficiently, and in a more elegant way, those molecules whose MPD in a single frequency field requires very high fluence. Trifluoromethane-T, a small molecule, has a 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, e.g. deuterium [15, 16], tritium [11], sulphur [17] and carbon [18].

In our recent work we have observed a remarkable improvement in T/H selectivity by multiple-frequency CO_2 laser irradiation of CHF_3/CTF_3 mixtures [19]. Irradiation was carried out at the Q branch of the v_2 absorption band of CTF_3 by various R branch lines of the 9.6 µm band of a CO_2 laser. Single line irradiation was carried out from the $9R(8)$ to $9R(26)$ lines while

multiline irradiation was carried out in two groups of lines, namely (i) 9R(8), 9R(10), 9R(12), 9R(14) and (ii) 9R(20), 9R(22), 9R(24), 9R(26). A tenfold improvement in selectivity was noticed on simultaneous irradiation by a group of lines of a 8.5 Torr CHF_3/CTF_3 mixture in the presence of argon at 20 Torr.

Most of the studies on fluoroform have concentrated on H/T separation; there are not many reports involving D/T separation using this system. Therefore in the present studies we investigated D/T separation using a multiple-frequency excitation scheme. In the CHF_3/CTF_3 system all irradiations were carried out in the Q branch of the v_2 absorption band of CTF_3, where the molecule has a good absorption. However, in the present case, due to expected interference from CDF_3 (see discussion below) CTF_3 excitation was carried out in the P branch of the v_2 mode. Some studies were also carried out in the Q branch of CTF_3 in order to compare the CDF_3/CTF_3 system with CHF_3/CTF_3.

1. Experimental

Trifluoromethane-T (CTF_3) was prepared by deuterium isotope exchange of CDF_3 (Matheson, 99% purity) with tritiated heavy water in the presence of dimethyl sulphoxide-d and sodium hydroxide-d by a method similar to the one reported in [3]. Typically the CDF_3 sample used in our experiments had 0.2 ppm CTF_3.

A 0.5 Hz repetition rate 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 cm^2) was formed with a Littrow mounted blazed grating and a Ge output mirror ($R = 10$ m). The principle of multiline operation of the laser is shown in Fig. 1 and discussed in detail elsewhere [19]. The pulse energy was measured by a pyroelectric joule meter (Lumonics 20D). The shot-to-shot variation in pulse energies was within ±5%. Laser frequencies were measured by a spectrum analyzer (Optical Engineering Inc.).

All irradiation was carried out at room temperature in a Pyrex cell (30 cm long 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 BaF_2 lens ($f = 25$ cm). Excitation in the v_2 absorption band of CTF_3 in a mixture of 2 Torr of CDF_3 (0.2 ppm CTF_3) with various amounts of Ar was carried out using different rotational lines in the R and P branches of the 9.6 μm band of the 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 microsecond long tail after the initial laser pulse. However, a small amount of nitrogen in the gas mixture was found to be efficient for obtaining better pulse energy in the case of multiple-frequency emission. Using a photon drag detector (Rofin), the temporal profiles of the laser pulses were found to be 100 ns FWHM in both cases.

Irradiated samples were cryogenically transferred to a radio-gas chromatograph (radio-GC) for analysis. The radio-GC consisted of a commercial Shimadzu GC-R1A (Porapak Q column, 5 mm i.d., 2 m long, 45 °C) equipped with thermal conductivity detector (TCD) and an indigeneously built proportional counter (10 ml, 3 kV) [20] for the analysis of tritium-bearing species. The depletion in CTF_3 and CDF_3 could be independently and simultaneously measured by the counter and the TCD, respectively. The C_2F_4 peak was also used to countercheck the CDF_3 dissociation. The determinations of CDF_3 and CTF_3 were reproducible within ±1% and run-to-run reproducibility was ±5%.

2. Results

The frequency dependence of CTF_3 MPD was determined at discrete frequencies of the CO_2 laser [from 9P(8) to 9P(24) in the P branch and at 9R(8) to R(12) in the Q branch] in the v_2 absorption profile. The cell-averaged dissociation probabilities per pulse $d_{T,D}$ were given by $d_{T,D} = -[\ln(1 - X_{T,D})]/n$ where $X_{T,D}$ denotes the dissociated fractions of T- and D-containing species after n pulses of irradiation and the ratio d_T/d_D gives the process selectivity $S_{T/D}$. These quantities were measured for various pulse energies and sample pres-
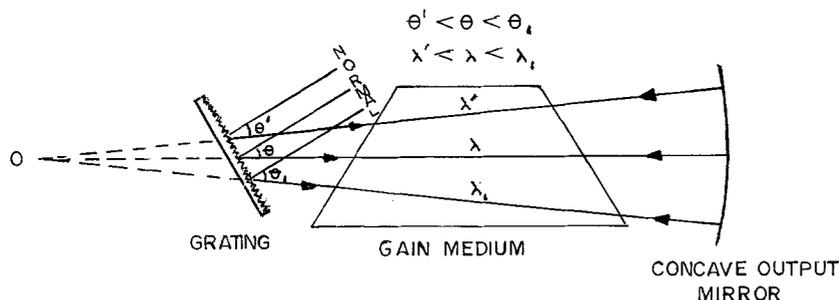

Fig. 1. Schematic of multiple frequency generation in a TEA CO_2 laser. Due to the concave geometry of the output mirror, the resonance condition is simultaneously satisfied for several frequencies

GRATING   GAIN MEDIUM

CONCAVE OUTPUT MIRROR

$\theta' < \theta < \theta_1$
$\lambda' < \lambda < \lambda_1$

Table 1. Frequency dependence of $d_{T,D}$ and $S_{T/D}$ in the IRMPD of CDF_3 at 2 Torr containing 0.2 ppm CTF_3 with 20 Torr of argon under single- and multiple-frequency excitation with total pulse energy of 1 J

Run No.	Line	Frequency [cm^{-1}]	$d_D \times 10^5$ (per pulse)	$d_T \times 10^5$	$S_{T/D}$
1	9P(8)	1057.30	0.94	6.01	6.39
2	9P(10)	1055.62	0.74	8.55	11.50
3	9P(12)	1053.92	0.72	9.34	13.01
4	9P(14)	1052.19	1.15	7.80	6.78
5	9P(16)	1050.44	1.12	7.70	6.90
6	9P(18)	1048.66	0.62	5.32	8.57
7	9P(24)	1043.16	0.04	2.32	58.0
8	9R(12)	1073.27	9.48	20.29	2.14
9	9R(10)	1071.88	6.53	16.0	2.45
10	9R(8)	1070.46	3.80	11.0	2.89
11	9P(8) to 9P(14)		1.08	12.94	11.98
12	9P(22) to 9P(28)		<0.04	< 0.04	–
13	9R(8) to 9R(14)		4.94	14.65	2.96
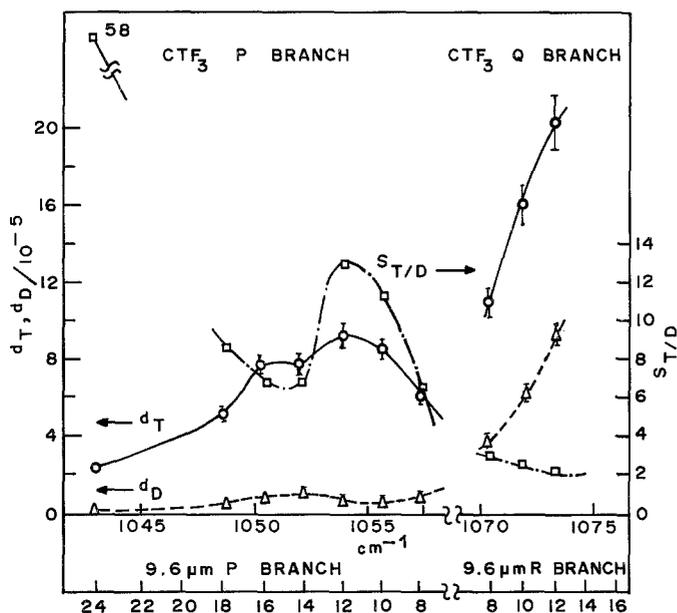
Fig. 2. Frequency dependence of the cell-averaged dissociation probability per pulse, $d_T(\circ)$ and $d_D(\triangle)$ under single-frequency excitation. The right-hand ordinate plots the single step selectivity factor defined as $S_{T/D}(\square) = d_T/d_D$. Sample: 2 Torr of CDF_3 containing 0.2 ppm CTF_3 and 20 Torr of argon at room temperature; pulse energy: 1 J

Figure 2 shows the MPD spectra of CTF_3 and CDF_3 (using single-colour irradiation, 1 J pulse energy) in 2 Torr of CDF_3 (containing 0.2 ppm CTF_3) with 20 Torr of Ar. With the present laser setup and irradiation geometry the focal fluence was estimated to be ≈ 175 J cm^{-2}. In the frequency range studied here, $d_{T,D}$ and $S_{T/D}$ (Fig. 2) are in excellent agreement with the IR absorption spectra of the system [21].

Table 1 shows d_T, d_D, and $S_{T/D}$ values for single-frequency and multiple-frequency excitation. Two groups of lines (i) 9P(8), 9P(10), 9P(12), 9P(14), (ii) 9P(22), 9P(24), 9P(26), 9P(28) in the P branch and one group of lines 9R(8), 9R(10), 9R(12), 9R(14) in the Q branch of CTF_3 were chosen for excitation. As can be seen from the table, in all cases selectivity remained almost constant compared to single-frequency excitation. The sample pressure and the fluence condition were identical in single- and multiple-frequency excitation. In the latter case, the total pulse energy of 1 J is distributed over the four frequencies.

3. Discussion

From the photochemical viewpoint of separation of lighter isotopes by MPD, absorption selectivity is one of the factors determining the practical success of the separation. However, other process parameters like gas handling (including expansion, compression and drying), D/T exchange, and stripping of TF may determine the overall economics of the scheme. The value of the optical selectivity is decided by the spectroscopic interference from the undesired species in the region of excitation of the desired species. For

sures. It was found that d_T had 3/2 power dependence with pulse energy E. While both d_T and d_D increased with increasing E, the selectivity $S_{T/D}$ decreased. With an increase in sample pressure, the selectivity was found to decrease due to different rates of increase in d_T and d_D. Parametric studies with the addition of argon to the mixture indicated a maximum selectivity with 20 Torr of argon for 2 Torr of mixture and therefore further studies were carried out with such a system.

the CHF_3/CTF_3 system under CO_2 laser excitation in the Q branch of the v_2 mode of CTF_3 (which is essentially $^{12}CTF_3$ at this low concentration), i.e. $1076.9 \, cm^{-1}$, the closest interfering $^{13}CHF_3$ absorption (Q branch $1115.9 \, cm^{-1}$) lies $39 \, cm^{-1}$ away [21]. However, in the CDF_3/CTF_3 system, $^{13}CDF_3$ interferes more strongly in the MPD process. The $v_2 \leftarrow 0$ Q/P peaks are situated at $1076.9/1061$ and $1089.8/1066.6 \, cm^{-1}$ for $^{12}CTF_3$ and $^{13}CDF_3$, respectively. Even the residual absorption of the more abundant species $^{12}CDF_3$ (Q branch $1111.2 \, cm^{-1}$) at the exciting laser frequency can degrade the selectivity severely (ratio of the strength of the CDF_3 feature to its CTF_3 analogue is 1.2 for the $v_2 \, Q$ branch peak). Thus for the CDF_3/CTF_3 system under single-frequency MPD one expects a poorer selectivity than for the CHF_3/CTF_3 system. However, we carried out MPD in the Q and P branches of CTF_3 absorption, and results indicated a better process selectivity in the P branch irradiation, which is further away from the CDF_3 absorption.

In experimental conditions similar to those of the present studies, the CHF_3/CTF_3 system exhibited a good selectivity at 8.5 Torr sample pressure under the excitation in the Q branch of CTF_3 [19]. However, when the CDF_3/CTF_3 mixture was irradiated at 8.5 Torr, no isotopic selectivity could be observed in $CTF_3 \, v_2$ mode excitation (even in the P branch). In this system we could observe the process selectivity when the sample pressure was kept around 2 Torr. This observation indicated the extent of interference from the undesired species in the CDF_3/CTF_3 system in the process selectivity.

As can be seen from Table 1, Q-branch excitation produced good yield but the selectivity was poor (run 8). For excitation in the P branch of CTF_3 (runs 1–6) the selectivity was improved but the yield was poor, due to the lower absorption of CTF_3 at these frequencies. In the red wing of the P branch (run 7) the selectivity was very good but the MPD yield was too small to have any practical importance. Compared to the Q-branch excitation, this set of experiments required a much larger number of pulses in order to produce measurable dissociation and to allow one to estimate the selectivity. These experiments were repeated with a high repetition rate (10 Hz) Lambda Physik CO_2 laser (Model EMG 201-E-CO_2) and the results were reconfirmed.

It is generally observed that as intensity increases the absorption of the undesired species becomes significant, leading to a reduction in isotopic selectivity. Nevertheless, the laser intensity cannot be reduced indefinitely below the MPD threshold, with the aim of improving the selectivity. Quack and Seyfang [22] have experimentally shown that for small molecules

like CF_3I, nonlinear intensity dependence of MPD becomes more pronounced at off-tuned frequencies. Hence by reducing the laser intensity the rate of MPD of off-tuned molecule reduces more than that of the tuned ones. 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 step. 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].

This technique was applied in the case of the CHF_3/CTF_3 system to observe any enhancement of process selectivity. Total pulse energy of a single line of a laser was distributed on 4 neighbouring lines and a tenfold improvement in the selectivity was noticed [19]. However, when this principle was extended to the CDF_3/CTF_3 system, no noticeable enhancement in T/D selectivity could be observed. For multiple-frequency irradiation using $9R(8)$ to $9R(14)$ in the Q branch of CTF_3, the selectivity remained similar to that of single-frequency excitation (compare run 13 with run 8). The selectivity remained almost constant even for excitation in the P branch using the $9P(8)$ to $9P(14)$ group of lines (compare run 11 with runs 2 and 3), however, excitation at the red wing of the P branch using $9P(22)$ to $9P(28)$ did not yield any measurable dissociation. This trend of selectivity could be understood from the earlier discussion on relative spectral features of the different species. Due to the closeness of $^{13}CDF_3$ and $^{12}CTF_3$ absorption features, on going from single-line to multiline operation the rates of MPD of both species were probably affected to a similar extent, and hence the effect of multiline excitation on the selectivity was probably too small to be detected by our apparatus. Therefore any enhancement of the selectivity, if observed at all, can be expected at the red wing of the P branch of CTF_3, but owing to the very small rate of MPD a very large number laser pulses will be required in order to measure the yield. Such experiments are extremely difficult and impractical with our low repetition rate laser.

These observations are similar to those reported by Magnotta and Herman [6] based on the spectroscopic information available in [21]. It was proposed in [21] that first removing photochemically the interfering ^{13}C isotopic species (1.1% natural abundance) may further increase the selectivity in the CHF_3/CTF_3 system, but this will probably not improve CDF_3/CTF_3 selectivity. Lack of any enhancement in selectivity even under off-tuned multiple-frequency irradiation in the present studies indicates strong

spectral interference from CDF_3 in CTF_3 MPD, and therefore we believe that the removal of ^{13}C species in this system will not be of any practical benefit.

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