Separation of Tritium from Deuterium by Pulsed NH_3 Laser-Selective Multiple Photon Dissociation of $CTCl_3$

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Abstract. The multiple photon dissociation of ppm level $CTCl_3$ in $CDCl_3$ and the selectivity of T/D separation were investigated using a pulsed ammonia laser. The effect of laser frequency, fluence and buffer gas pressure on the dissociation rate and isotopic selectivity were studied. The depletion of $CDCl_3$ was not observed within experimental errors. A lower limit of single step selectivity factor was found to be > 5000 at 133 Pa substrate pressure.

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The issue of removing tritium from contaminated light and heavy water in fission reactor operation and reprocessing of spent fuel has been studied for the past decade. Since then research and development of both laser and conventional non-laser methods of tritium recovery have been quite active. Progress in laser isotope separation (LIS) of tritium has been dramatic since the successful demonstration of T/H and T/D separation using infrared multiphoton dissociation (IRMPD) of halogenated alkanes [1–8]. An exhaustive review of the present status in this field has been given by Herman et al. [9]. The tritium removal is accomplished through two successive steps: The tritium is transferred from contaminated water (HTO, DTO) to an appropriate working molecule followed by its removal by IRMPD of the molecule and the whole cycle can be repeated. Therefore it is important that a working molecule for LIS not only dissociates with high isotopic selectivity but also rapidly exchanges with tritium in water. From this view point, chloroform has been shown to be most promising working molecule for T/D separation. However, there are not many studies on this system compared to the exhaustive studies on CO_2-laser-induced MPD of fluoroform system [10–17]. The studies on chloroform so far include T/H separation [18] and T/D separation [6, 19, 20] using an ammonia laser. These investigations on T/D recovery dealt with high T/D fraction (200 ppm and upwards) in low pressure (26.6 Pa) $CTCl_3/CDCl_3$ mixtures. However, the typical T/D fraction in a heavy-water fission reactor tritium recovery plant is of the order of 5 ppm. In the present studies, we have investigated T/D recovery using chloroform system having a T/D fraction in this range

(1 ppm) at moderate pressure (up to 400 Pa). In earlier investigations, the ammonia laser employed required a filter cell [19, 21] to block the residual pumping CO_2 laser beam which resulted in reduction in useful energy and also some uncertainty about the frequency of the ammonia laser [18]. The present parametric studies on $CTCl_3/CDCl_3$ mixtures employed an indigenous NH_3 laser where such difficulties were avoided by spatially separating the CO_2 pump beam from the NH_3 laser beam.

1. Experimental

Tritiated chloroform ($CTCl_3$) was obtained by the base-catalysed isotope exchange reaction between $CDCl_3$ (99.8% D) and tritiated heavy water. 5 ml of tritiated heavy water (DTO of specific activity 7.5 mCi/ml), 10 ml of $CDCl_3$ and 0.3 ml of 11 M NaOD were stirred in a vacuum-tight pyrex bulb for 4 h at room temperature. The top water layer was removed by slow pippeting. The remaining tritiated $CDCl_3$ was purified by passing through a molecular sieve 5 A column. The specific activity of chloroform thus obtained was about 0.4 mCi/ml which corresponds to about 1 ppm of $CTCl_3$ in $CDCl_3$.

A Lumonics 103-2 grating tuned TEA CO_2 laser operating at a 0.5 Hz repetition rate was used to pump the ammonia laser. The experimental arrangement is shown in Fig. 1. The pump laser was operated in the TEM_{00} mode using an intracavity aperture. The laser delivered typically 2–3 J in 100 ns (FWHM) pulses with 1 µs tail on the 9 µm R-branch lines. The grating G delivers the pump
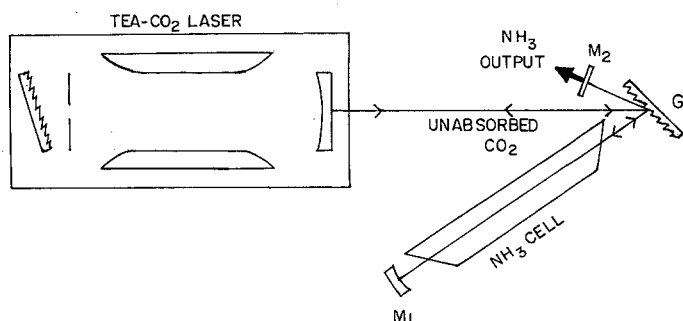
Fig. 1. Schematic of line tunable ammonia laser; M_1: concave gold mirror (5 m radius of curvature); M_2: output mirror; G: grating

beam [9R(30)] into the ammonia laser cavity formed by an output mirror M_2 (43% reflectivity at 12 μm) and a 5 m radius of curvature concave gold mirror M_1. NH_3 is contained in a 120 cm long, 25 mm internal diameter pyrex cell fitted with ZnSe Brewster windows at both ends. The pulse energy was measured by a pyroelectric joule meter (Lumonics 20 D). The ammonia laser frequencies were measured by a calibrated IR monochromator. The temporal profiles of the pump and ammonia laser beam were monitored with a fast photoresister detector. The ammonia laser output energy depended on operating conditions such as NH_3/N_2 ratio, total pressure and the temporal shape of the CO_2 laser pulse. Under optimum operating conditions, the maximum energy obtained in 7 mm diameter beam was about 200 mJ per pulse in a 200 ns FWHM pulse with one microsecond tail using 1:250 NH_3/N_2 gas mixture at 8 kPa total pressure. The efficiency of this laser with respect to the NH_3/N_2 mixture ratio, temporal shape of CO_2 laser beam, etc., has been discussed elsewhere [22].

All irradiations were carried out at room temperature in a Pyrex cell (10 cm in length and 1.5 cm in diameter) equipped with the ZnSe windows and a greaseless stopcock. Focussing of the laser beam was done at the centre of the cell by using either 5 cm or 10 cm focal length ZnSe lens. After photolysis, the sample was cryogenically transferred to the gas sampling loop of a gas chromatograph (Shimadzu GC-R1A) equipped with 1.2 m long Porapak Q column (80–100 mesh, 3 mm i.d.). The depletion of $CDCl_3$ was determined by the thermal conductivity detector. The activity measurement of $CTCl_3$ using gas flow proportional counter employed in our earlier studies on fluoroform system [15–17] was found to be severely distorted due to the quenching effect of the corresponding deuterated species. Therefore we employed the procedure of Yokoyama et al. [18] for measuring the depletion of $CTCl_3$. The effluent from the gas chromatograph was bubbled through 10 ml of toluene contained in a scintillation vial cooled at −10° C for trapping chloroform. Gas chromotraphic analysis of chloroform condensed in toluene by the above bubbling procedure indicated quantitative dissolution of chloroform in toluene. To this solution 5 ml of 0.034 M 2,5-diphenyloxazone in toluene was added and the activity measured using a liquid scintillation counter (Packard Tri-carb 4530). In blank runs, it was established that non-tritiated $CDCl_3$ under simi-

lar conditions did not show any activity and the $CTCl_3$ activity was seen to be independent of $CDCl_3$ concentration. Variations of less than ±1% were obtained in the determination of tritium activity in chloroform.

2. Results and Discussion

2.1 Frequency and Pressure Dependence of the Dissociation Rate

The (0,0) band peak of the $CTCl_3$ v_4 mode is located at 835.3 cm^{-1} [6]. The dependence of $CTCl_3$ MPD on NH_3 laser frequency was determined in the v_4 absorption profile. The cell averaged dissociation rate $d_{T,D}$ 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. In none of these experiments was $CDCl_3$ decomposition observed. The d_T values showed a maximum near 12.08 μm (828 cm^{-1}) which matches with the result obtained by Magnotta et al. [19].

The dependence of the $CTCl_3$ dissociation rate on $CDCl_3$ pressure is shown in Fig. 2 using the 833 cm^{-1} NH_3 laser line at a pulse energy of 150 mJ. The dissoci-
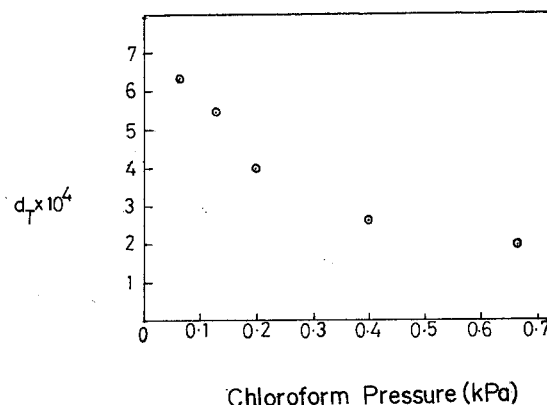

Fig. 2. Dependence of $CTCl_3$ dissociation rate on chloroform pressure (10 cm focal length lens, 150 mJ at 833 cm^{-1})
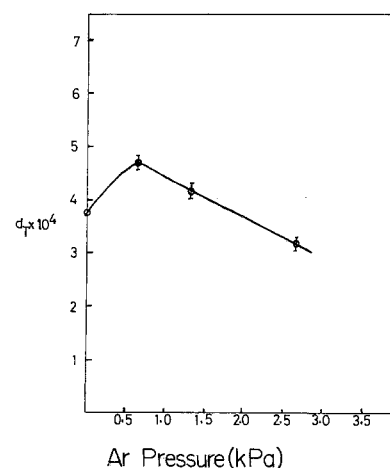

Fig. 3. Dependence of $CTCl_3$ dissociation rate on argon pressure (chloroform pressure = 133 Pa, 5 cm focal length lens, 150 mJ at 833 cm^{-1})
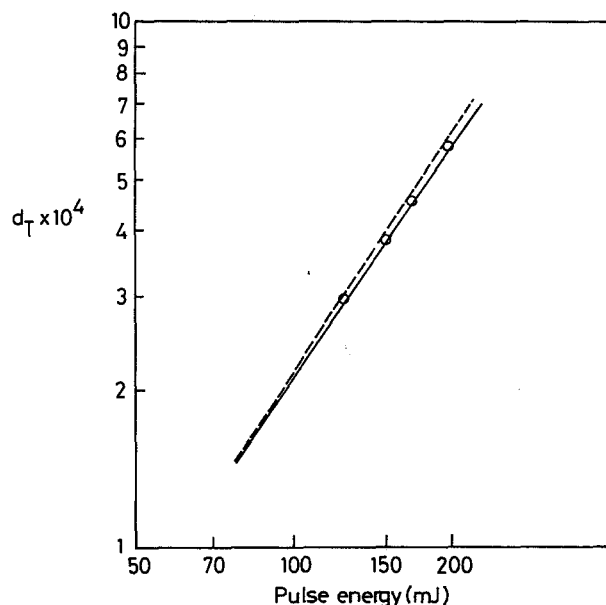
Fig. 4. Variation of $CTCl_3$ dissociation yield with pulse energy at $833 \, cm^{-1}$ (5 cm focal length lens, 133 Pa chloroform pressure). The solid and the dotted curves represent the best fit results by assuming Gaussian and uniform beam profiles, respectively

ation rate was found to decrease as the $CDCl_3$ pressure increased. This is due to the vibrational relaxation of $CTCl_3$ by collision with $CDCl_3$. These studies did not reveal any multiphoton absorption (MPA) bottleneck presumably because of the lower fluence used. However, such a bottleneck was evidenced by the upturn in the yield vs. pressure curve using buffer gas. Irradiation of a 133 Pa $CTCl_3/CDCl_3$ mixture in presence of various amounts of argon as buffer gas showed an initial maximum followed by a gradual decrease in the dissociation rate (Fig. 3). The maximum in the yield curve at argon pressure around 665 Pa indicated the removal of the MPA bottleneck while the subsequent decrease is due to the vibrational deactivation of $CTCl_3$ by collisions with Ar. Since there was no evidence of dissociation of nonresonant $CDCl_3$ molecules, dissociation selectivity was enhanced during the initial increase in d_T.

2.2 Fluence Dependence of Dissociation Rate

The fluence dependence of $CTCl_3$ dissociation rate is shown in Fig. 4. The data were obtained by irradiation

of a 133 Pa $CTCl_3/CDCl_3$ mixture using $833 \, cm^{-1}$ NH_3 laser line using a 5 cm focal length lens. Use of a 10 cm focal length lens indicated better dissociation rate presumably because of an increase in the irradiation volume, while working with fluence well above the critical fluence.

To assess the spatially averaged data obtained in such focussed geometries quantitatively, various models have been used [9, 10, 23–25] to describe the dependence of dissociation probability as a function of fluence. These models are very useful for design of any practical LIS system. The dissociation rate d is obtained from the integration of the dissociation probability $D(\phi, v)$ over the entire cell volume and is expressed as

$$d = 1/V \int_{vol} D(\phi, v) dV,$$

where ϕ and v are the working laser fluence and frequency respectively. The dissociation probability at a given frequency is assumed to have the following widely accepted power law form:

$$D(\phi) = (\phi/\phi_c)^m \quad \text{for} \quad \phi \leq \phi_c$$
$$= 1 \quad \text{for} \quad \phi > \phi_c,$$

where ϕ_c is the critical fluence above which the dissociation probability is unity. In the power-law model, two important criteria like optical thickness of the sample and the transverse beam profile of the laser have to be considered for analytical functions to be evaluated. Since the $CTCl_3$ concentration is very small, an optically thin condition is a good approximation. The NH_3 laser employed here delivered a multimode output beam which can be asumed to have transversely uniform or flat-top profile. Under these conditions, following the treatment of Takeuchi et al. [10] and Yokoyama et al. [18], the critical fluence ϕ_c and the exponent m were calculated from the energy dependent dissociation rate data. The data for the irradiation of 133 Pa $CTCl_3/CDCl_3$ mixture at $828 \, cm^{-1}$ fitted well with the assumed values of $\phi_c = 21 \pm 2 \, J/cm^2$ and $m = 3$, under the uniform beam profile approximation. For other sample pressures and buffer gas pressures these values are listed in Table 1. For the sake of comparison, we have also evluated these parameters for the case of a Gaussian laser beam. The dotted and solid curves in Fig. 4 represent the best fit results by assuming uniform and Gaussian beam profile, respectively.

Table 1. Model parameters and selectivity values for $CTCl_3$, MPD

Sample pressure [Pa]		Laser frequency [cm^{-1}]	ϕ_c [J · cm^{-2}] [a]		$d_T \times 10^4$ [pulse^{-1}]	Selectivity [b] $S = d_T/d_D$
Chloroform	Ar		U ($m = 3$)	G ($m = 3$)		
133	0	828	21 ± 2	22 ± 3	10.14	5070
133	0	833	30 ± 2	30 ± 3	5.82	2910
200	0	833	37 ± 3	40 ± 4	4.28	2140
400	0	833	50 ± 5	53 ± 5	2.83	1415
133	665	833	22 ± 2	23 ± 2	7.31	3655

[a] Values are obtained by assuming uniform (U) and Gaussian (G) beam profile
[b] Selectivity values are obtained for 200 mJ pulse energy and using upper limit of d_D value i.e., 2.0×10^{-7} per pulse

2.3 Isotopic Selectivity

The ratio of the dissociation rates d_T/d_D is a measure of the process selectivity. Although we have been able to dissociate $CTCl_3$ very efficiently in all the runs, the dissociation of $CDCl_3$ could not be determined. Even after 10000 irradiation pulses, we could not get any evidence for dissociation of $CDCl_3$. Therefore, the lower limit of the selectivity can be conservatively estimated from the detection limit of the gas chromatographic (GC) method. The GC analysis of the standard mixture of $CDCl_3$ and the photolysis product C_2Cl_4 showed that at 62.5 Pa sample pressure in the cell, products arising out of 0.4% decomposition of $CDCl_3$ could have been observed. Taking this value for d_D calculation, selectivity factors have been obtained in neat and buffer systems [cf. Table 1]. It should be noted that in all these studies, the number of irradiating pulses was chosen so as to yield about 50% $CTCl_3$ dissociation.

3. Conclusion

The isotopically selective multiphoton dissociation of $CTCl_3$ at ppm level in $CDCl_3$ was investigated using the CO_2-laser-pumped NH_3 laser. Using appropriate amounts of the buffer gas, the dissociation yield and the selectivity can be further improved. The critical fluence for the MPD of $CTCl_3$ was found to be $21 \pm 2\,J/cm^2$ at 133 Pa substrate pressure. The determination of the selectivity factor was conservatively estimated by the uncertainty in the measurement of $CDCl_3$ dissociation. A selectivity factor > 5000 has been obtained by irradiating $CDCl_3$ (1 ppm $CTCl_3$) at 133 Pa with the 12.08 μm NH_3 laser. Judging from the high selectivity factor, relatively low critical fluence and fast tritium exchange reaction between $CDCl_3$ and DTO, we believe that the chloroform system is very promising for a practical tritium recovery plant.

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