

Selective ir Laser Chemistry of CDF_3 in Natural Fluoroform

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Abstract. Selective decomposition of CDF_3 at natural abundance level (≈ 150 ppm) in fluoroform has been achieved by infra-red multiple-photon excitation at moderate substrate pressure using 100 ns FWHM CO_2 laser pulses. Effects of energy fluence, number of laser pulses, buffer gas pressure and substrate pressure on decomposition yield and bulk selectivity are reported and discussed.

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IR laser chemistry of CDF_3 has been an exciting area in relation to Laser Isotope Separation (LIS) of deuterium [1]. Studies on fluoroform enriched in CDF_3 have yielded promising results. A logical extension would be selective dissociation of CDF_3 present at natural abundance level (≈ 150 ppm) in fluoroform. This has been achieved by employing very short duration pulses (< 10 ns FWHM) with selectivity factor of ≈ 2000 at ≈ 100 Torr substrate pressure [2]. In such a fast excitation, collisions detrimental to selectivity through energy transfer processes will be absent. Our recent investigations on $\text{CDF}_3/\text{CHF}_3$ system have indicated that it is possible to work with conventional commercial TEA- CO_2 lasers (pulse duration ≈ 100 ns FWHM) and still minimise selectivity loss in moderate pressure ranges (10–20 Torr) by adding appropriate amounts of buffer gas [3]. Isotopic scrambling is reduced under this condition as the buffer gas quenches unwanted excitations. We have further extended this work to fluoroform containing ≈ 150 ppm CDF_3 and are able to achieve selective CDF_3 dissociation at this low level [4]. In the present investigation, D/H selectivity and yield were surveyed as a function of CHF_3/Ar composition, sample pressure, laser fluence and number of laser pulses.

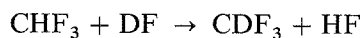
1. Experimental

A Lumonics 103-2 TEA- CO_2 laser tuned to $R(10)10.6 \mu\text{m}$ (969 cm^{-1}) was used for all irradiations.

The pulse energy was measured by a calibrated pyroelectric detector (Lumonics, 20 D). The laser beam was focussed at the centre of a pyrex reaction cell using a BaF_2 lens ($f = 50$ or 100 cm). The energy fluence at the focus was estimated from the laser-beam divergence of 1.7 mrad and the laser input energy.

Concentration of CHF_3 (Matheson, purity $> 99\%$) was determined from quantitative ir spectrophotometry (Perkin Elmer, 180). Also, decomposition in CHF_3 was monitored by a quadrupole mass spectrometer (Extranuclear Laboratories Inc., EMBA II) by measuring the m/e ratio at 40 and 51 (Ar^+ and CHF_2^+ ions, respectively) for the irradiated sample and comparing it with that of a reference sample. This enabled us to monitor any change in CHF_3 concentration larger than $\pm 1\%$.

Decomposition in CDF_3 was measured by a novel method [3]. DF, the photodecomposition product from CDF_3 , attacks the pyrex cell and produces an equivalent amount of deuterated water, which is adsorbed on cell walls. It is to be noted that the possible loss of DF due to exchange reaction with natural fluoroform, viz.,



has been proved to be unimportant [1c]. After photolysis is over, both CHF_3 and Ar are carefully removed. A known amount of dry NH_3 (10–20 Torr) is introduced into the cell from a NH_3 reservoir bulb and allowed to equilibrate with the deuterated water

overnight. Since CDF_3 content of the working mixtures is only a few mTorr, the quantity of $\text{D}_2\text{O}/\text{HDO}$ produced is extremely small, and it results in rapid exchange reactions with added large excess of NH_3 . Under this condition, "D" from adsorbed water is quantitatively exchanged with the "H" of the bulk gaseous NH_3 . NH_2D content of this NH_3 and that of the reservoir NH_3 is determined by a (D/H) isotopic ratio measuring mass spectrometer (Technical Physics and Prototype Engineering Division, BARC, 6-60) with an accuracy of $\pm 1\%$. This instrument is of the double collector type and has an on-line furnace for reducing NH_2D and NH_3 at 700°C into HD and H_2 [5]. The increase in NH_2D content of NH_3 , which has been exposed to a photolysis cell, can be correlated to a CDF_3 decomposition in the following manner:

The atom fraction ratio of reservoir NH_3 , $(\text{D}/\text{H})_0$, in parts per million (ppm), is given by

$$(\text{D}/\text{H})_0 = [\text{No. of } \text{NH}_2\text{D molecules} / (3 \times \text{No. of } \text{NH}_3 \text{ molecules})] \times 10^6. \quad (1)$$

Let N_D be the quantity of CDF_3 decomposed in a photolysis run giving rise to an equivalent amount of DF species and p_{NH_3} be the pressure of NH_3 added to the photolysis cell. The atom fraction ratio of NH_3 exposed to the photolysis cell, $(\text{D}/\text{H})_1$, is given by

$$(\text{D}/\text{H})_1 = [(N_D^0 + N_D) / N_H^0] \times 10^6 \text{ ppm}, \quad (2)$$

where

$$N_D^0 = 3 \times (\text{D}/\text{H})_0 \times p_{\text{NH}_3} \times 10^{-6} \text{ Torr}, \quad (3)$$

$$N_H^0 = 3 \times p_{\text{NH}_3} \text{ Torr}. \quad (4)$$

Thus by measuring $(\text{D}/\text{H})_0$, $(\text{D}/\text{H})_1$ and p_{NH_3} , N_D can be found, which directly gives the total quantity of CDF_3 decomposed after m pulses.

The reliability of the chemical exchange method was counterchecked by ir spectrophotometry for $\text{CDF}_3/\text{CHF}_3$ synthetic mixture photolysis wherein the CDF_3 concentration permitted independent monitoring by the latter method.

2. Results and Discussion

Photolysis of natural fluoroform was carried out either in neat form or in Ar mixture for various parametric conditions. Since different cells were used for different focussing optics, the CDF_3 dissociation extent in each experiment is described in terms of "reaction volume per pulse, V_R " for uniform comparison. V_R is given by

$$V_R = \text{specific dissociation rate} \times \text{cell volume}. \quad (5)$$

The specific dissociation rate of CDF_3 or CHF_3 (i.e., d_D or d_H) is given by

$$d = [1/m] \times [\ln(N_0/N)], \quad (6)$$

where N_0 and N being the initial and final concentration of CDF_3 or CHF_3 , respectively, after m pulses. The bulk selectivity factor for the process is defined as

$$S = d_D/d_H. \quad (7)$$

2.1. Effect of Number of Pulses

For a satisfactory determination of V_R for CDF_3 , each experiment was conducted typically with 6000 pulses. In the low-fluence range ($10\text{--}20 \text{ J cm}^{-2}$), V_R remained almost constant independent of the number of laser shots. However, at higher fluence, increasing the number of pulses seemed to reduce V_R . For example, at 2000 pulses, $V_R = 8.3 \times 10^{-2} \text{ cm}^3 \text{ pulse}^{-1}$ but reduced to 5.8×10^{-2} at 6000 pulses for focal fluence of 110 J cm^{-2} . This could be attributed to a progressive depletion of CDF_3 .

2.2. Effect of Laser Fluence

A set of preliminary experiments was carried out to characterise the dependence of MPD yield of CDF_3 , present at 150 ppm natural abundance, on fluence. Figure 1 shows the V_R obtained with 1:1 CHF_3/Ar mixture photolysis at a total pressure of 45 Torr, when

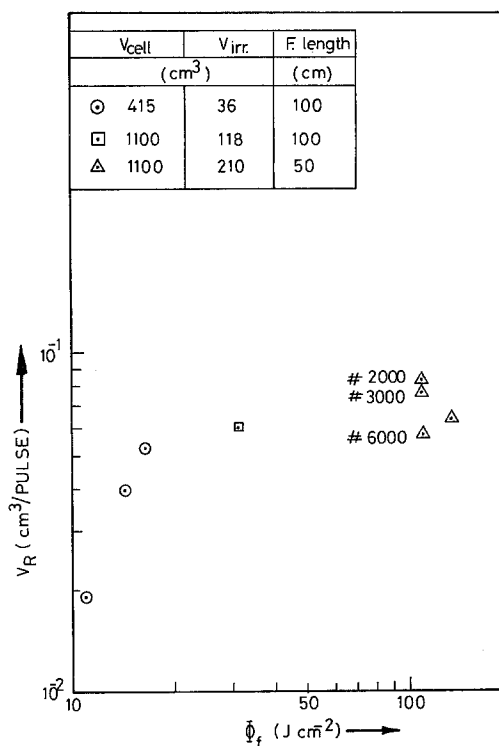


Fig. 1. Dependence of V_R on focal fluence in 1:1 CHF_3/Ar mixture photolysis at 45 Torr total pressure. At $\phi_f = 110 \text{ J cm}^{-2}$, effect of number of irradiation pulses on V_R is shown (see text)

the focal fluence ϕ_f was varied between 10 and 130 J cm^{-2} . For low fluences ($10\text{--}20 \text{ J cm}^{-2}$), V_R varied as $E^{2.5}$. Using the deconvolution technique [6], a combination of "critical fluence" ϕ_c for CDF_3 MPD of 50 J cm^{-2} and an "order of multiphoton process", $n=3$, fitted the data satisfactorily. For photolysis of neat CHF_3 at 25 Torr, critical fluence for CDF_3 MPD was estimated to be $\approx 110 \text{ J cm}^{-2}$. Thus, Ar addition significantly lowers the critical fluence. It is quite promising because fluence requirement for CDF_3 decomposition by conventional 100 ns FWHM CO_2 laser has now become comparable to 30 J cm^{-2} reported for excitation with short pulse width ($< 10 \text{ ns}$) CO_2 laser [2a]. The higher fluence experiments were conducted using a different cell and a 50-cm focal-length lens. Respective cell volumes and irradiated beam volumes for different focussing optics are shown in the figure inset. The higher fluence studies were done with a view to increase the yield which, however, remained practically constant.

2.3. Effect of Pressure

Increase in total pressure resulted in a decrease of V_R almost linearly at constant ϕ_f for both neat CHF_3 as well as 1:1 CHF_3/Ar mixture photolysis (Fig. 2). This is due to collisional quenching of vibrationally excited molecules. Figure 2 also shows the decomposition

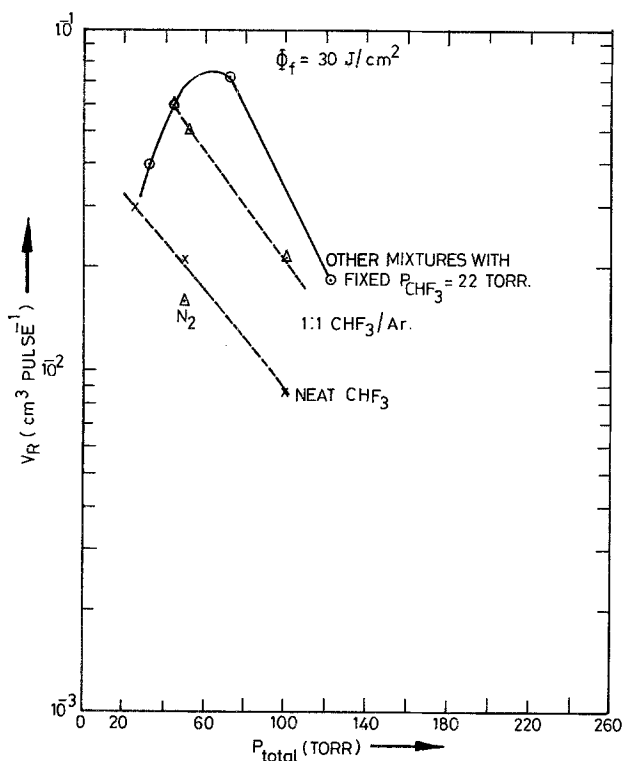


Fig. 2. Dependence of V_R on pressure in the photolysis of neat CHF_3 and CHF_3/Ar mixtures at 30 J cm^{-2} focal fluence

yield, when Ar was added progressively to CHF_3 kept at 22 Torr.

The yield curve can be seen to rise initially for low Ar pressure (≤ 50 Torr) and then falls off at higher pressures. At present, there is a qualitative understanding of the effect of collisions between resonant molecule and buffer gas in multiphoton excitation and dissociation processes. It is a common opinion that this increase is due to a "rotational hole-filling" mechanism [7]. Due to the Boltzmann distribution of molecules over the rotational levels of the ground vibrational states, the monochromatic laser radiation excites just a small portion of molecules, q , from a single or small set of rotational levels. The portion of interacting molecules depends on the spectral width (typically $\approx 0.03 \text{ cm}^{-1}$ for CO_2 laser lines) and the intensity of the exciting radiation. The key factor q may be expressed as a statistical sum of rotational states Z_{rot} , the sublevel degeneracy g , and the energy E_{rot} . For simple and light molecules, q usually varies between 10^{-1} and 10^{-2} . For molecules like CDF_3 whose rotational constant ($B=0.33 \text{ cm}^{-1}$) has a high value, the q -factor is generally smaller compared to that for larger polyatomics like SF_6 .

At high photon fluxes ($\phi_f \geq 10 \text{ J cm}^{-2}$) used in these experiments, population of a small set of rotational levels addressed by the laser is quickly depleted, i.e., a hole is burnt. Further excitation is possible only when lower levels are repopulated and upper levels depleted by rotational relaxation. Collisions with non-polar buffer gas dominated by a dipole-induced dipole interaction during the course of the laser pulse ($\approx 100 \text{ ns}$) tend to redistribute the rotational population to bring more molecules into resonance with the excitation field (i.e., there is an increase in the so-called q factor). Rotational relaxation for CDF_3 -inert gas (with typical " $p\tau$ " value of $\approx 100 \text{ ns Torr}$) is faster than the gas-kinetic collision rate [8], and thereby improves the dissociation yield considerably. Although the dependence of V_R on Ar pressure is slower than linear, it does not contradict the decisive effect of rotational relaxation. The possibility of some molecules being "sticked" at intermediate levels with $E \leq E_c$ (quasi-continuum) for small species like CDF_3 cannot be excluded [9].

With further increase in buffer-gas pressure the vibrational deactivation process becomes important, which can compete with radiative excitation. Meanwhile, the increase in yield due to rotational relaxation ceases at some pressure; the reason is just that the rise of q is saturated. Thus for $p > p_q$ (saturation), the primary effect of collisions is to remove energy from the excited parent molecules via $V-T$ processes, thereby reducing both the average level of excitation and the dissociation yield. Use of nitrogen as buffer gas was

Table 1. Specific decomposition rates and bulk selectivity factors in natural fluoroform

Run no. ^a	Pressure [Torr]		Specific decomposition rate (10^{-6} per pulse)		Bulk selectivity factor, $S = d_D/d_H$
	CHF ₃	Buffer	CDF ₃ (d_D)	CHF ₃ (d_H)	
1	25	0	27.2	< 1.68	> 16.0
2	100	0	7.0	< 1.68	> 4.2
3	22	10	36.4	< 1.68	> 21.7
4	22	22	54.8	< 1.68	> 33
5	22	22	48.2	< 1.68	> 28.5
6	22	50	65.5	< 1.68	> 40
7	22	100	16.3	2.8	5.8
8	25	25	14.8	7.3	2.0
9	50	50	17.3	3.7	4.6

^a Focal fluence was 30 J cm^{-2} in all runs except in 5 and 9. It was 110 and 125 J cm^{-2} in 5 and 9, respectively. In run Nos. 3–7 and 9, the buffer gas was Ar. In 8, it was N₂

found to be less effective than Ar. At 50 Torr total pressure, photolysis of a 1 : 1 CHF₃/N₂ mixture resulted in lower V_R as well as lower S compared to that of 1 : 1 CHF₃/Ar mixture (run No. 8 in Table 1).

2.4. Isotope Selectivity

In most of the irradiations, the CHF₃ concentration remained practically unchanged within statistical error limit of $\pm 1\%$ for both ir spectrophotometry and mass spectrometry. This means that the specific dissociation rate d_H for CHF₃ should be less than 1.68×10^{-6} per pulse for 6000 pulses of irradiation. Table 1 gives the lower-bound bulk selectivity factor S for various experimental conditions. The collisional processes, which define the dissociation yield $V_R[p(\text{Ar})]$ have an effect on S , i.e., $S[p(\text{Ar})]$. At $p(\text{Ar}) \leq 50$ Torr, it is rotational relaxation that has a main effect on the variation of S . The highest value, $S > 40$, was obtained in 1 : 2 CHF₃/Ar mixture. S was found to decrease with increasing substrate pressure (run No. 2), buffer-gas pressure (run No. 7) and fluence (run Nos. 5 and 9). It was quite dependent on the nature of buffer gas (compare run No. 4 with No. 8).

Formation of deuterated water in the photolysis cell due to DF/HF reaction with pyrex cell body was confirmed by monitoring the HDO signal using a semiconductor diode laser (SDL) spectrometry (Laser Analytics Inc., LS-3). Briefly, the experiment involved introducing a small, measured quantity of water in the photolysis cell after irradiation and removal of undecomposed mixture. After allowing the water to equilibrate with the deuterated water product, the increase in SDL signal of HDO compared to natural level at 1271.6 cm^{-1} was monitored. Addition of external water was essential for ease of detection of HDO signal and required a minimum 3 Torr H₂O pressure for a path length of 5 m.

Conclusions

All these results demonstrate that isotope selective ir MPD of CDF₃ is possible even at natural abundance level in fluoroform with conventional 100 ns FWHM CO₂ laser pulses. A moderate yield and selectivity could be obtained by judicious choice of substrate/buffer-gas pressure and laser fluence.

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