

IR LASER PHOTOLYSIS OF CDF₃: ROLE OF BUFFER GAS ON SELECTIVITY AND YIELD FOR DEUTERIUM ENRICHMENT IN FLUOROFORM

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Summary

The isotope selectivity and specific decomposition rates for the IR multiphoton dissociation of CDF₃-CHF₃ mixtures were examined as functions of various experimental parameters such as substrate pressure, composition, laser energy, irradiation geometry and buffer gas pressure. The isotopic scrambling observed with a 100 ns CO₂ laser pulse at moderate pressures of the mixture was shown to be reduced by the addition of appropriate amounts of the buffer gas argon.

1. Introduction

Selective IR multiphoton dissociation (IRMPD) of fluoroform-*d* (CDF₃) in fluoroform (CHF₃) by a transversely excited atmospheric pressure (TEA) CO₂ laser continues to be an attractive option for deuterium enrichment [1 - 5]. The IR absorption coefficient of CDF₃ exceeds that of CHF₃ by a factor of about 2000 in the wavelength region of 10.2 - 10.3 μm of the CO₂ laser [1]. The IR absorption band of CDF₃ at about 10.3 μm is due to the C-D wagging mode, while the corresponding band in CHF₃ shifts to 7.3 μm [6]. Although the 2ν₆ mode of CHF₃ lies at about 10.3 μm, direct excitation of this overtone transition can be ignored because of its extremely weak absorption compared with that of CDF₃.

Very high selectivities in this system have been reported under two conditions, *i.e.* irradiation of the substrate at (i) very low pressure (a few millitorrs) with a 100 ns (full width at half-maximum (FWHM)) CO₂ laser pulse [3] and (ii) high pressure (about 100 Torr) with an ultrashort CO₂ laser pulse (less than 10 ns) [4, 5]. The selectivity in the IRMPD process usually decreases with increasing substrate pressure [7], primarily because of vibrational energy transfer between resonantly excited and off-resonant

molecules. Isotope scrambling in the CHF_3 system as a result of other processes such as secondary radical reaction [8] has been proved to be unimportant. The above mentioned two cases of high selectivity experiments utilized this fact, and collision-induced energy transfer processes [9,10] were minimized by employing either a very low pressure or an ultrashort laser pulse width.

However, recent work has demonstrated that the moderate substrate pressure (about 10 - 20 Torr) and 100 ns FWHM pulse available in a normal commercial TEA CO_2 laser could be employed, and such scrambling processes can be controlled by using a buffer gas. It has been shown that the addition of argon as a buffer gas in the IRMPD of CTF_3 (parts per million level) in CHF_3 increases the specific decomposition rate for CTF_3 and the overall selectivity [11, 12]. Similar trends have been observed in the IRMPD of the $\text{CDCl}_2\text{F}-\text{CHCl}_2\text{F}$ system in the presence of argon [13]. Even though it has been reported that the addition of 30 Torr of argon improves the dissociation yield by a factor of 100 in a system containing 66 mTorr of CDF_3 [1], investigations of its effect on the selectivity of this important system are still warranted [12].

In the present work we have examined the effect of argon on the selectivity and yield for deuterium enrichment in the $\text{CDF}_3-\text{CHF}_3$ system at moderate pressures using a 100 ns FWHM CO_2 laser. Similar approaches have been used for ^{13}C enrichment [14, 15], where selectivity enhancement was obtained with increasing substrate pressure. However, the major difference is that these studies did not make use of any buffer gas but were carried out using off-resonant wavelength excitation at very low fluence. In this paper we report the dependence of the dissociation yields and selectivities of 1:4 and 1:84 $\text{CDF}_3-\text{CHF}_3$ systems upon the pulse energy, irradiation geometry, sample pressure and buffer gas pressure.

2. Experimental details

2.1. Irradiation conditions and sample handling

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. This line is resonant with the ν_5 C—D wagging mode of CDF_3 . The temporal profile, as monitored using a photon drag detector (Rofin model 7415), consisted of a 100 ns spike followed by a tail of a few microseconds. After passing through an aperture 2 cm in diameter the laser pulse was suitably attenuated in energy by polythene strips whenever necessary and was focused at the centre of a cylindrical reaction cell. The incident energy of the beam striking the front window of the cell was measured using a calibrated pyroelectric detector (Lumonics model 20D). Depending on the focusing optics employed (BaF_2 lens of focal lengths f of 10, 25 and 50 cm), three different Pyrex cells (volumes of about 110 cm^3 , 240 cm^3 and 330 cm^3 with irradiation path lengths of 9.5 cm, 31 cm and 41 cm

respectively) were used. In a typical experiment the focal fluence was estimated from the laser beam divergence (about 1.7 mrad) and the input laser energy. Commercial samples of CDF_3 (Merck, Sharp and Dohme; atom fraction of deuterium, about 98%) and CHF_3 (British Oxygen Ltd.) were used after purification by trap-to-trap distillation. Argon (Airco; minimum purity, 99%) was used as received. Typically, 2000 - 3000 pulses were used in each experiment.

2.2. Analysis

The CDF_3 and CHF_3 concentrations were determined by quantitative IR spectrophotometry (Perkin-Elmer spectrophotometer models 577 and 180) with a typical reproducibility of better than $\pm 1\%$. CDF_3 was monitored using the ν_5 band at 980 cm^{-1} and CHF_3 was monitored at two different bands, *i.e.* the ν_1 band (C-H stretching mode) at 3034 cm^{-1} and the ν_4 band (C-H rocking mode) at 1377 cm^{-1} [6]. Decomposition in CDF_3 as observed by IR analysis was checked by a chemical exchange procedure, which is described briefly below.

The photoproduct DF of the IRMPD of CDF_3 attacks the Pyrex cell and produces an equivalent amount of deuterated water which is physically adsorbed on the cell walls. The deuterium content of the water produced in this way is quantitatively determined by introducing a known amount of dry ammonia gas into the cell, allowing it to undergo deuterium exchange with the final product, *i.e.* water, and determining the increase in the NH_2D content of NH_3 by quantitative mass spectrometry. The mass spectrometer (model 6-60 supplied by the Technical Physics and Prototype Engineering Division, Bhabha Atomic Research Centre) used in our experiments for the analysis of the $[\text{D}]/[\text{H}]$ ratio in NH_3 is of the double-collector type and has an on-line uranium furnace for reducing NH_2D and NH_3 at $700\text{ }^\circ\text{C}$ to HD and hydrogen for isotopic analysis [16]. It is routinely used to determine the $[\text{D}]/[\text{H}]$ ratio in water, ammonia and hydrogen samples with an accuracy to better than 0.5% at the natural abundance level of deuterium.

There was good agreement between the values obtained for CDF_3 decomposition by the exchange method and IR spectrophotometry whenever the CDF_3 concentration was sufficient to obtain an IR spectrum. In a 1:84 CDF_3 - CHF_3 mixture (about 100 mTorr of CDF_3), the CDF_3 dissociation yield was exclusively followed by the chemical exchange method. This method is particularly suited for quick evaluation of CDF_3 decompositions at low levels. Even in the case of CHF_3 decomposition, which can be separately followed by IR spectrometry, CDF_3 depletion can be determined by this method without interference.

3. Results and discussions

The photolysis of either neat CDF_3 or a CDF_3 - CHF_3 mixture was investigated as a function of the incident laser energy, the focusing optics,

the buffer gas pressure and the composition of the mixture. Since different cells had to be used for different focusing optics, the CDF_3 dissociation yield in each experiment is described in terms of the reaction volume per pulse V_R for uniform comparison; V_R is given by

$$V_R = \text{specific dissociation rate} \times \text{cell volume} \quad (1)$$

The specific dissociation rates d_D and d_H of CDF_3 and CHF_3 respectively are given by

$$d = \frac{1}{n} \ln\left(\frac{N_0}{N_n}\right) \quad (2)$$

where N_0 is the initial concentration of CDF_3 or CHF_3 and N_n is the final concentration after irradiating with n pulses. The bulk selectivity factor for the process is defined as

$$S = \frac{d_D}{d_H} \quad (3)$$

3.1. Photolysis of neat CDF_3

3.1.1. Effect of pulse energy

Irradiation of 2 Torr of neat CDF_3 using the lens with $f = 25$ cm and various pulse energies of the R(10) $10.6 \mu\text{m}$ line showed that the dissociation follows the $3/2$ power law. Specific dissociation rates d_D for resonant CDF_3 increased with pulse energy E_0 : $d_D \propto E_0^{1.6 \pm 0.1}$ (Table 1, runs 1 - 5). The value of the critical fluence F_c^D for unit dissociation probability in the laser beam volume for CDF_3 is evaluated using (i) the formula for a dog-bone geometry [17] and (ii) the deconvolution method described by Takeuchi *et al.* [12] for the condition where the focal fluence F is greater than the critical fluence F_c^D . The two procedures gave the same value of F_c^D for CDF_3 ($49 \pm 4 \text{ J cm}^{-2}$ at 2 Torr pressure). A similar value was obtained by

TABLE 1

Effect of pulse energy and focal length of the lens in the IR multiphoton dissociation of neat CDF_3 (2 Torr)

Run	Incident energy E_0 (J)	Focal length of the lens f (cm)	Reaction volume V_R ($\times 10^{-3} \text{ cm}^3 \text{ pulse}^{-1}$)
1	0.30	25	3.3
2	0.43	25	5.7
3	0.66	25	10.5
4	0.84	25	15.0
5	1.10	25	24.0
6	1.0	10	8.3
7	1.0	25	20.5
8	1.0	50	30.0

Marling *et al.* [4] at a pressure of 2 Torr, whereas at 66 mTorr sample pressure F_c^D was increased to 180 J cm^{-2} [1]. The considerable reduction in F_c^D at torr levels of CDF_3 can be attributed to the collision-assisted removal of the rotational bottleneck.

3.1.2. Irradiation geometry

These experiments were carried out with the aim of optimizing the optics for better yields at a fixed incident energy. Table 1 (runs 6 - 8) shows the effect of varying the optics on V_R at a fixed incident energy of 1 J pulse^{-1} for the photolysis of 2 Torr of neat CDF_3 . The results indicate that a higher reaction volume could be obtained by employing loose focusing optics. However, a limiting reaction volume which is insensitive to further increases in focal length seems to be occurring presumably because the fluence necessary for driving the CDF_3 decomposition reaches threshold values at boundaries of approximately the same volume.

It has been observed that dissociation of non-resonant molecules decreases with a reduction of focal fluence [18]. In order to take advantage of any such benefits offered by loose optics on isotopic selectivity, all irradiation experiments with dilute 1:84 CDF_3 - CHF_3 mixtures were carried out with the $f = 50 \text{ cm}$ lens (focal fluence, 90 J cm^{-2} (see Section 3.2)) while the $f = 25 \text{ cm}$ lens was used in other experiments. An additional benefit of employing loose optics is that high sample pressures can be irradiated without laser-induced dielectric breakdown.

3.1.3. Effect of added argon

Figure 1, curve a, shows that addition of argon increases V_R ; this result is similar to that reported by Herman and Marling [1] except that in the

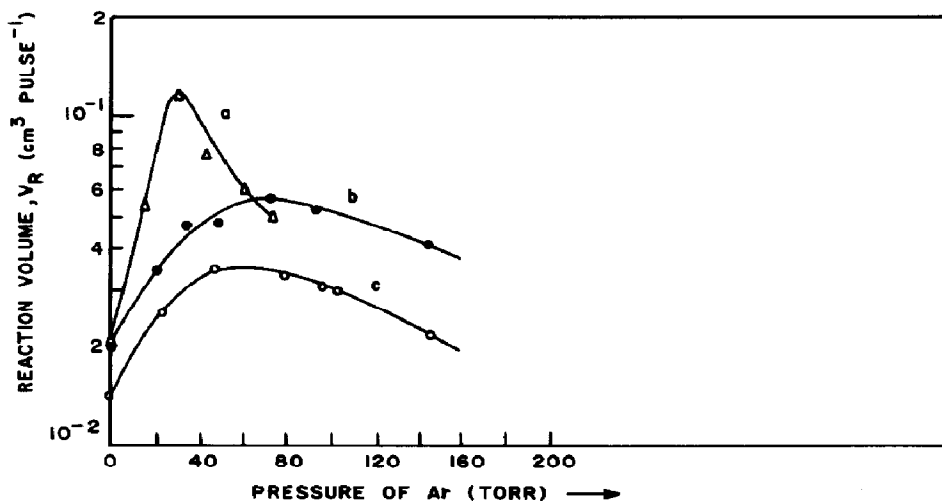


Fig. 1. Dependence of the decomposition yield of CDF_3 in neat form and in CDF_3 - CHF_3 mixtures on the argon pressure: curve a, neat CDF_3 ($p = 2 \text{ Torr}$, 175 J cm^{-2}); curve b, 1:4 mixture ($P_{\text{CDF}_3} = 0.4 \text{ Torr}$, 175 J cm^{-2}); curve c, 1:84 mixture ($P_{\text{CDF}_3} = 0.1 \text{ Torr}$; 90 J cm^{-2}).

present work pressures in the range of torrs of CDF_3 are employed in contrast with the millitorr pressures employed in ref. 1. A substantial sixfold improvement in V_R could be obtained by using a focal fluence of 175 J cm^{-2} at argon pressures of about 30 Torr. However, at higher argon pressures a sharp decrease in the yield was noticed. Dielectric breakdown was observed at $P_{\text{Ar}} > 75$ Torr. The value of F_c^D for CDF_3 in the presence of the optimum argon pressure was $15 \pm 2 \text{ J cm}^{-2}$.

The beneficial effect of argon can be understood in terms of the rotational relaxation of ground state molecules via $\text{CDF}_3\text{-Ar}$ collisions which enhances the multiphoton absorption (MPA) and MPD [1]. Collisions may also enhance MPD by promoting vibrational-vibrational intramolecular energy transfer enabling the moderately excited molecules to absorb more photons. The observed decrease in V_R at higher argon pressures is ascribed to the decrease in the vibrational energy content of CDF_3 molecules due to enhancement in the vibrational-translational relaxation rates.

3.2. Photolysis of $\text{CDF}_3\text{-CHF}_3$ mixtures

3.2.1. Effect of added CHF_3

With a view to studying the effect of CHF_3 on CDF_3 decomposition yield and isotopic selectivity, the experiments were performed using various compositions of $\text{CDF}_3\text{-CHF}_3$. The decomposition yield of CDF_3 first increases with CHF_3 pressure, reaches a maximum at about 1 Torr CHF_3 and then decreases as the CHF_3 pressure is further increased (Fig. 2).

3.2.2. Effect of added argon

Similar to the case of neat CDF_3 , V_R for the mixtures increases with the addition of argon, reaches a maximum and then decreases at higher argon pressures. The conditions employed and the results obtained are shown in Fig. 1. In general the V_R values for the 1:84 mixture (Fig. 1, curve c) are

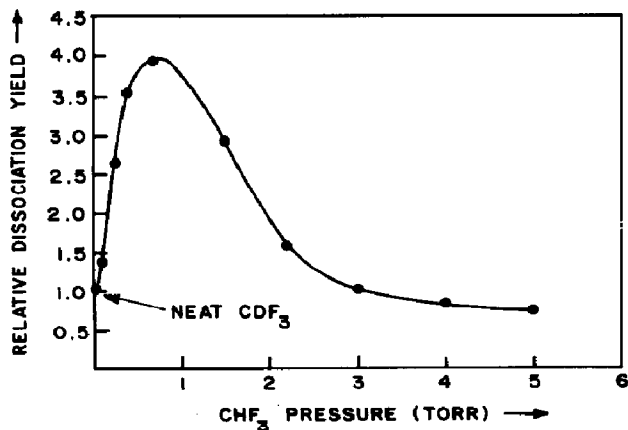


Fig. 2. Dependence of the relative decomposition yield of CDF_3 in the presence of CHF_3 : CDF_3 pressure, 0.1 Torr; focal fluence, 175 J cm^{-2} .

smaller than those of the 1:4 mixture (Fig. 1, curve b) and reflect the deactivation of vibrationally excited CDF_3 by CHF_3 . Although the concentrations of CDF_3 are quite small in these mixtures (P_{CDF_3} of 0.1 Torr and 0.4 Torr respectively), V_R for these mixtures is comparable with that of 2 Torr of neat CDF_3 . For the conditions in Fig. 1, curve a, the higher fluence and higher substrate pressure employed partially remove the ground state rotational bottleneck and thereby reduce the requirement of the number of collisions between CDF_3 and argon for maximizing MPA and MPD as compared with the mixture systems. This explains the better yield shown in Fig. 1, curve a, at relatively low argon pressures.

The critical fluence F_c^D for the 1:84 mixture has a fairly high value of $130 \pm 5 \text{ J cm}^{-2}$. With the addition of about 50 Torr of argon, F_c^D can be decreased to $90 \pm 5 \text{ J cm}^{-2}$. At the substrate pressure employed (8.4 Torr) the decomposition of CHF_3 could not be detected within the accuracy of the IR spectrometer (1% change). However, when the substrate pressure was increased to 16.5 Torr dissociation of CHF_3 could be observed and F_c^H for CHF_3 dissociation in the 1:84 mixture was estimated to be $220 \pm 10 \text{ J cm}^{-2}$ which was further increased in the presence of 50 Torr of argon (the critical fluence for CHF_3 was estimated as in ref. 12 using $n_H = 3$). Therefore, with added argon in the 1:84 mixture, the d_D value increases while the d_H value decreases resulting in improvement of the selectivity of the IRMPD process.

3.2.3. Isotopic selectivity

Very high enrichment factors have been reported for the IRMPD of CDF_3 in CHF_3 at low pressures [3]. However, higher pressure can be employed without selectivity loss only by using a laser pulse of short duration [4, 5]. Ishikawa and coworkers [9, 10] have observed severe selectivity loss with a 1:1 CDF_3 - CHF_3 mixture in the pressure range of 2 - 10 Torr with an 80 ns FWHM laser pulse.

The present work demonstrates that the addition of argon overcomes some selectivity loss in the moderate pressure range using a conventional 100 ns FWHM CO_2 laser pulse. Table 2 contains the results of the experiments in the 1:84 mixture. In the absence of argon, the increase in substrate pressure resulted in a loss of selectivity (compare run 1 with run 4) owing to vibrational-vibrational energy transfer from the excited CDF_3 to the major component CHF_3 molecules resulting in dissociation of the acceptor molecule. The addition of argon increases d_D marginally but decreases d_H considerably and therefore enhances the selectivity factor (compare run 1 with run 2 and run 4 with runs 5 and 6).

Sugita *et al.* [13] have shown in the photolysis of the 1:1 CDCl_2F - CHCl_2F system that the addition of argon has only a slight effect on the specific dissociation rate of CDCl_2F whereas the corresponding rate for CHCl_2F decreases resulting in enhancement of the bulk selectivity factor. The present system of a CDF_3 - CHF_3 mixture irradiated with the R(10) $10.6 \mu\text{m}$ CO_2 laser line is analogous to the CDCl_2F - CHCl_2F system rather than the CTF_3 - CHF_3 system [12]. The major difference in the role of argon

TABLE 2

Specific decomposition rates and lower limits of selectivity for 1:84 CDF₃-CHF₃ mixtures

Run ^a	Substrate pressure (Torr)	Argon pressure (Torr)	Specific decomposition rate (×10 ⁻⁵ pulse ⁻¹)		Lower limit of bulk selectivity factor $S = d_D/d_H$
			CDF ₃ (d_D)	CHF ₃ (d_H)	
1	8.4	0	4.27	0.335 ^b	12
2	8.4	48	10.5	0.335 ^b	31
3 ^c	8.4	48	26.6	0.335 ^b	80
4	16.5	0	9.6	2.0	5
5	16.5	50	14.0	1.7	8
6	16.5	104	13.3	0.335 ^b	40

^aThe focal fluence is 90 J cm⁻².

^b d_H values correspond to a higher estimate than the actual values as the determination of d_H is limited by the detection limit of IR spectrometry (1% change).

^cA higher focal fluence of 130 J cm⁻² was used.

in the CDF₃-CHF₃ and CTF₃-CHF₃ systems is its ability to affect d_H . In the former the decomposition of CHF₃ is essentially due to vibrational-vibrational intermolecular energy transfer from CDF₃, and argon effectively deactivates such indirect vibrational excitation of CHF₃ and thereby decreases d_H . In CTF₃-CHF₃ the irradiation frequency employed was also absorbed by CHF₃ and such direct excitation is assisted by the addition of argon. This was reflected in the increase of d_H as reported by Takeuchi *et al.* [12].

The quenching of unwanted excited species, preferably by use of buffer gas, is rather similar to the approach used in ¹³C enrichment [14, 15] wherein a higher substrate pressure resulted in better selectivity with reduced yield. The result was interpreted in terms of different quenching efficiencies or different energy transfer rates between molecules in discrete states and molecules in quasi-continuum states.

Ishikawa *et al.* [9] have discussed the mechanism of isotope scrambling in CDF₃-CHF₃ mixtures and concluded that the selectivity S is related to the internal-energy-dependent unimolecular rate constant K_2 for CDF₃* and the intermolecular vibrational-vibrational transfer rate constant K_{3b} for energy transfer to CHF₃:

$$S = 1 + \frac{K_2/K_{3b}}{[\text{CDF}_3]}$$

Our experimental results suggest that for the 1:84 CDF₃-CHF₃ mixture $K_2 \approx 10^6$ s⁻¹, corresponding to the absorption of three excess photons. This value can be compared with $K_2 \approx 10^7$ s⁻¹ and the absorption of five excess photons by CDF₃ in the 1:1 CDF₃-CHF₃ mixture studied by Ishikawa *et al.* [9].

The addition of argon to the mixture results in (i) enhanced energy absorption by CDF_3 owing to rotational hole filling and as a consequence a higher value for K_2 and (ii) additional quenching of both CDF_3^* and CHF_3^* in collision with argon. Processes (i) and (ii) have an opposing influence on the net accumulation of vibrational energy in CDF_3 whereas process (ii) is detrimental to CHF_3 decomposition. It is therefore possible to choose an optimum range of buffer gas pressure to increase the relative rates of the decomposition of CDF_3 - CHF_3 and thus to achieve an enhancement in selectivity. The maxima observed in Fig. 1 represent such optimum buffer gas pressure ranges under the fluence and composition conditions studied.

From considerations such as those given above, a few experiments carried out with 10 - 20 Torr natural CHF_3 demonstrated that selectivity factors higher than 100 could be obtained in the presence of argon using a 100 ns FWHM CO_2 laser for irradiation.

4. Conclusions

Enhancements in the dissociation yield and selectivity were achieved in the dilute CDF_3 - CHF_3 system in the moderate pressure range with a 100 ns pulse by using argon as the buffer gas. From the previous [12, 13] and present studies, it appears that enhancement of isotopic selectivity by buffer gas can be obtained by judicious choice of substrate/buffer gas pressure, laser frequency and fluence.

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