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IR FLUORESCENCE STUDIES OF THE IR MULTIPLE-PHOTON DISSOCIATION OF THE SYSTEM CDF_3–CHF_3

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Summary

Time-resolved IR emissions were obtained for IR multiple-photon excitation/dissociation of CDF_3 at 970 cm^{-1} in neat form and its mixtures with CHF_3 and argon at moderate pressures. Enhancements in emission intensities were observed for CDF_3^* and DF^* on addition of argon. The bimodal exponential decay observed for both CDF_3^* and DF^* emissions in the neat photolysis of CDF_3 changed into single-mode decay when the sample was irradiated in the presence of argon at a focal fluence of 95 J cm^{-2}. The bimolecular rate constant for collisional deactivation of CDF_3^* by argon was 1.3×10^3 s^{-1} $Torr^{-1}$. *In situ* selectivity factors were determined from the measurements of DF^* and HF^* emission intensities in the photolysis of 1:1 CDF_3–CHF_3 mixtures.

1. Introduction

Deuterium enrichment by CO_2-laser-induced multiple-photon dissociation (MPD) of CDF_3 in CDF_3–CHF_3 mixtures is a well-known application of the technique of laser isotope separation. The selective IR MPD is a result of the isotopic shift of approximately 100 cm^{-1} of the $\nu_5 \leftarrow 0$ band in CDF_3 and its strong absorption in the region 10.2 - 10.3 μm [1]. Single-step enrichment factors exceeding 20 000 [2, 3] and very large D/H selectivity in absorption have been reported [4]. It is encouraging that the photochemical process is simple and clean. The endothermicity of 20 300 cm^{-1} for HF (or DF) elimination, a dominant channel in the thermal decomposition of CHF_3 [5], is 16 900 cm^{-1} lower than that of the next most accessible channel of carbon–hydrogen bond scission [6]. The activation energy for the favoured three-centre HF elimination is 24 150 cm^{-1} [7]. Therefore, excess energy is available for partitioning among the products which can lead to the produc-

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tion of vibrationally excited HF (or DF). In MPD experiments, IR fluorescence at wavelengths characteristic of HF and DF have been observed [3, 8], and the formation of deuterated water from the reaction of DF and HF with a Pyrex photolysis cell has been reported [9, 10].

Although this evidence supports the simple picture of the dissociation route, the characterization of the excitation–dissociation process leading to excited parent and product molecules has not been investigated extensively. Secondly, the isotopic selectivity scrambling in CDF_3–CHF_3 mixtures, especially in moderate pressure regimes, can occur via V–V energy transfer between the resonant CDF_3 and non-resonant CHF_3 molecules [11]. It has been shown previously that the detrimental effects of collisions with CHF_3 can be avoided either by using short laser pulses [9, 12] or by beneficial buffer gas addition for excitation with pulses whose full width at half-maximum (FWHM) is 100 ns [10, 13]. In the present investigation, an IR fluorescence technique has been used to characterize the *in situ* fluorescence of the parent and product molecules in neat CDF_3 and in CDF_3–CHF_3 and CDF_3–Ar mixtures at moderate pressures. Parametric studies in which the substrate/buffer gas pressure and laser fluence were varied revealed the nature of the excitation–dissociation process. The role of argon in improving the selectivity can also be appreciated from these results.

2. Experimental details

All the experiments were performed with a static system at room temperature. The conventional set-up includes a photolysis laser, a cell and an IR detector with an appropriate signal processing system (*cf.* Fig. 1).
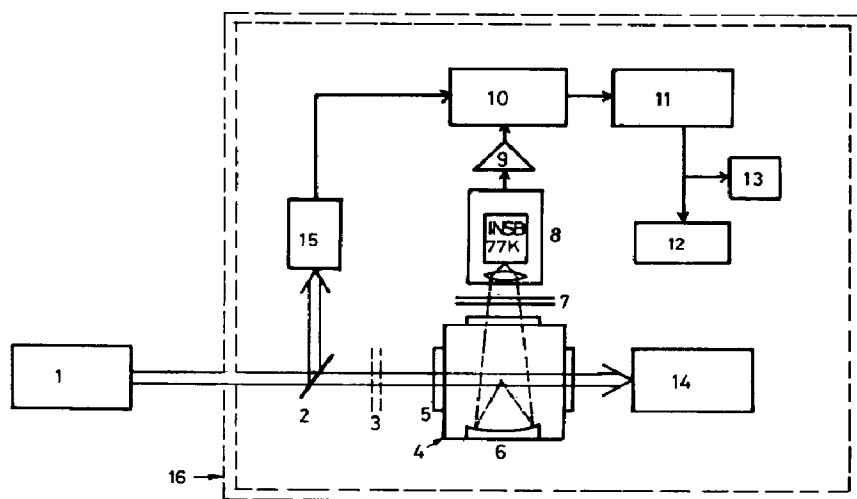

Fig. 1. Schematic diagram of the experimental set-up: 1, TEA-CO_2 laser; 2, beam splitter; 3, attenuators; 4, fluorescence cell; 5, BaF_2 windows; 6, gold-coated mirror; 7, bandpass filter; 8, InSb detector; 9, amplifier; 10, transient digitizer; 11, signal averager; 12, Y–T plotter; 13, cathode ray oscilloscope; 14, energy meter; 15, photon drag detector; 16, Faraday cage.

The photolysis/fluorescence cell was a 10 cm aluminium cube. Radiation from a pulsed CO_2 laser (Lumonics TEA-103-2) entered and exited through a pair of BaF_2 windows (5 cm in diameter). The fluorescence was collected at right angles to the laser beam by an $f/2$ gold-coated concave mirror of diameter 2 in. The radiation, after appropriate filtering with band-pass filters, was detected by an InSb detector (Judson Infrared Inc., J-10D, photovoltaic type) cooled at 77 K. The signals from the detector were amplified with a wide-band amplifier (PAR model-115) and digitized by a Biomation 8100 transient digitizer. The stored signal was transferred to a signal averager (Nicolet 1170) for repetitive measurements. The output of the averager was either displayed on an oscilloscope and photographed or plotted using a $Y-T$ chart recorder. The laser pulse picked up with a photon drag detector (Rofin model 7415) was used as a trigger for the transient digitizer. The overall time response of the system was about 1 - 2 μs but it was found to be susceptible to electrical interference from the laser. Therefore, the whole apparatus, apart from the laser, was contained in a Faraday cage to minimize electrical interference.

The irradiations were performed by two methods. An unfocused and collimated beam (cross-sectional area, about 0.8 cm^2) was used for studies of the fluorescence of parent molecules alone under a low fluence below the dissociation threshold. Fluorescence from both the parent and the products were investigated at higher fluence using a focused beam (BaF_2 lens, f = 10 cm) at the centre of the cell. The laser pulse consisted of a gain-switched pulse of 100 ns (FWHM) containing about two-thirds of the pulse energy followed by a tail of about 1 μs (FW). The pulse energy was varied by attenuating the beam with polyethylene sheets of the appropriate thickness. Commercial samples of CDF_3 (Merck, Sharp and Dohme; atom fraction of deuterium, about 98%) and CHF_3 (Matheson, purity better than 99%) were used after purification by trap-to-trap distillation. Argon (Airco, purity better than 99%) was used as received.

3. Results and discussion

3.1. Low fluence excitation of neat CDF_3

TEA-CO_2 laser irradiation of 10 Torr CDF_3 with the 10 R(10) line at 969 cm^{-1} in a fluence range up to 250 mJ cm^{-2} yielded IR fluorescence in the region 4 - 5 μm. This can be attributed to vibrationally excited CDF_3^* because the emission centre located around 4.4 μm coincides with the $v = 0 \rightarrow v = 1$ transition of the ν_1 C—D stretching mode [1]. The emission shows a relatively broad band which can be due to either several combination bands overlapping the C—D stretching band [8] or several $\Delta v = 1$ transitions among high vibrational levels ($v \geqslant 2$) in the same manifold. We believe that the broadening is caused by the transitions among highly excited levels in both ν_1 and the isoenergetic combinations manifold.

Figure 2 represents the transient profile of CDF_3^* fluorescence at 7 Torr. The temporal behaviour was found to be a weak function of CDF_3 pressure in the range 2 - 10 Torr. The rise of the signal was instantaneous and within the response time of the detection system. The observed profiles at various CDF_3 pressures seem to indicate that the total decay consists of two components: a fast-decaying component with a decay time $\tau_d = 4.5 \pm 1.5$ μs and a second slow component with $\tau_d = 50 \pm 10$ μs. With higher pressures the decay behaviour becomes more complicated, as reported by Ishikawa et al. [8]. The fast component arises from direct multiple-photon excitation of CDF_3, while the slower process is indicative of collisional excitation induced by V–V energy transfer between excited CDF_3 molecules. The fluence dependence of the peak intensity of emission revealed two regions. Initially the slope is 3 up to about 200 mJ cm^{-2} and afterwards it has a steep value of 7 for $\phi \geqslant 200$ mJ cm^{-2}. This indicates the overriding importance of the fluence to the multiple-photon excitation process.

3.2. High fluence IR MPD of neat CDF_3

At the higher fluence of 95 J cm^{-2} with the focused irradiation geometry, CDF_3 yielded IR emission over a wide wavelength region of 3 - 5 μm. The emission was assigned to highly vibrationally excited DF^* in the region 3 - 4 μm, while the parent molecule fluoresces in the vicinity of 4.4 μm as discussed above. Appropriate bandpass filters were used to separate the emissions of the different species.

The CDF_3^* emission, which is somewhat broader than the low fluence emission, was temporally resolved to characterize the decay process. As in the previous case, a bimodal decay pattern was observed with $(\tau_d)_{fast} = 4 \pm 1$ μs and $(\tau_d)_{slow} = 36 \pm 4$ μs for 7 Torr CDF_3 irradiated with $\phi_f = 95$ J cm^{-2} (cf. Fig. 3(a)). Although no definite conclusion can be drawn regarding the change in $(\tau_d)_{fast}$ because the time involved is close to the instrumental response time, there is a considerable reduction in τ_d for the slower component. This can be understood on the basis that under high fluence the average excitation is increased and subsequent collisional energy transfer occurs among relatively more highly vibrationally excited CDF_3^* compared with the low fluence case.
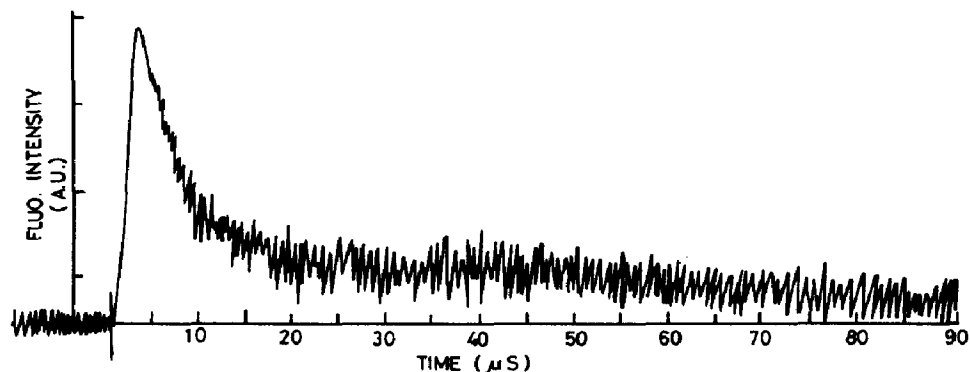

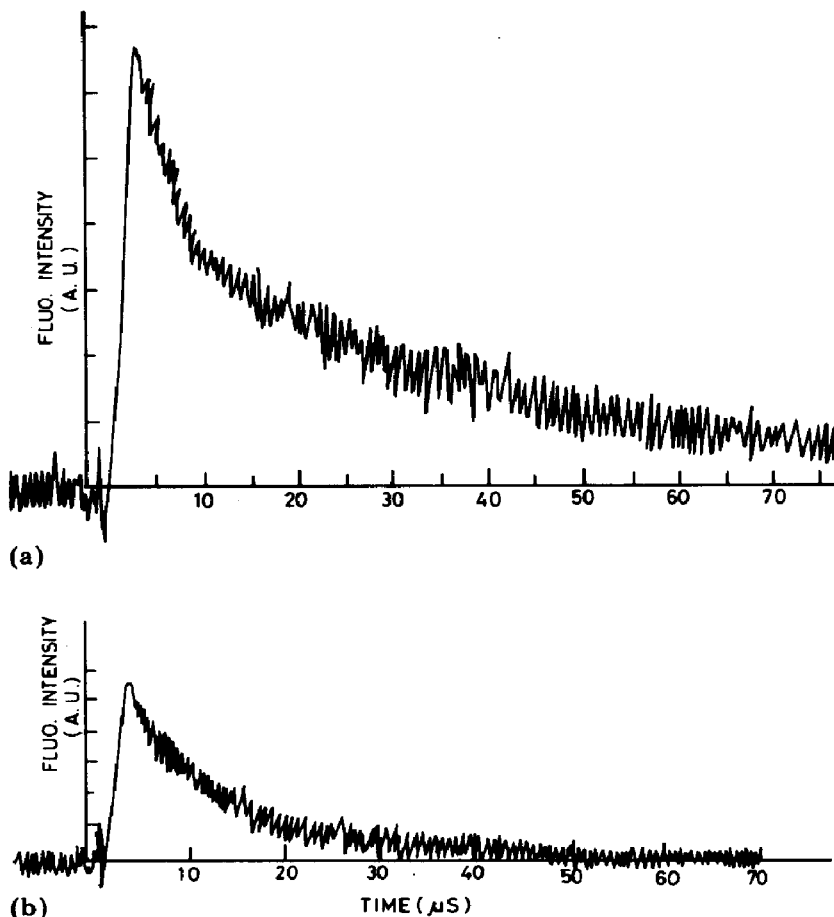Fig. 2. CDF_3^* emission at low fluence (300 mJ cm^{-2}) in 7 Torr neat CDF_3.

Fig. 3. IR fluorescence signals from neat CDF_3 at high fluence ($\phi_f = 95$ J cm^{-2}): (a) CDF_3^* emission; (b) DF* emission.

The DF* emission with two peaks in the region 3 - 4 μm was found to have bimodal temporal behaviour as reported previously [8]. In our measurements, we obtained $(\tau_d)_{fast} = 4 \pm 1$ μs and $(\tau_d)_{slow} = 18 \pm 2$ μs for irradiation of 7 Torr CDF_3 with a fluence of 95 J cm^{-2} (cf. Fig. 3(b)). The third component reported in ref. 8 was absent, probably because our substrate pressure was below 10 Torr.

The IR MPD of halogenated ethanes and ethylenes has been shown by several investigators [14, 15] to proceed mainly by elimination of a hydrogen halide molecule. The HF* vibrational energy distribution has been measured in many cases and has also been computer simulated [14 - 16]. Using a similar approach, comparison of the observed spectra with those for excited DF* reported or discussed in the literature indicates that the levels up to about $v = 3$ are significantly populated in the molecular elimination reaction. Clough et al. [17] and Berry [18] have shown that a statistical treatment is inadequate to describe the hydrogen halide level population in the four-

centre molecular elimination in the above-mentioned systems. The amount of excess energy available is not sufficient to populate higher vibrational levels of HF and can be explained on the basis of the composite effect of partitioning of the excess energy and fixed or localized energy associated with the transition state [14]. The results obtained so far indicate that vibrational excitation of HF, depending on the precursor, requires 16% - 31% of the fixed energy.

The reaction mechanism for the unimolecular decay of a molecule such as fluoroform depends on two factors, namely (i) the relative barrier heights for the possible processes and (ii) their statistical factors. A loose activated complex for a simple bond cleavage reaction, such as $CDF_3 \rightarrow CDF_2 + F$, is favoured statistically over a tight complex in the molecular elimination channel. However, the barrier height of the complex elimination channel is significantly lower than the bond cleavage process, which overcomes the statistical disadvantage at lower levels of excitation. Thus DF elimination is found to be the only product channel in MPD of CDF_3. Emissions due to HF* were not observed in IR MPD of a mixture of 5 Torr CDF_3 and 5 Torr H_2, and this corroborates the above conclusion.

The observed decay pattern reflects the temporal dependence of the process of formation of DF*. CDF_3 decomposes with a rate constant of 10^7 s^{-1} after being excited to a level which is five photons in excess of the dissociation threshold [11]. The fast decay is attributed to the DF* produced from such fast direct multiple-photon excitation (MPE) of CDF_3 during the laser pulse. On the post-pulse time scale, the molecules left at excitations less than five excess photons will then dissociate with a range of rates depending on the excitation levels. This highly vibrationally excited CDF_3* below the dissociation threshold can also contribute to DF* production via collisional V–V energy transfer. The slower decay in DF* emission can be attributed to the superposition of such processes.

3.3. Effect of argon addition

Addition of an inert buffer gas such as argon is known to enhance MPD of CDF_3 by a "rotational hole filling" mechanism, as was observed in static cell photolysis experiments [4, 10, 13]. This aspect was investigated in real time with a system containing 2 Torr CDF_3 by monitoring CDF_3* emission under conditions of both low and high fluence. Additionally the change in DF* emission on varying the argon pressure was monitored in high fluence dissociation experiments.

The results showed that the enhancement in emission intensity on addition of argon is more significant for low fluence irradiation than high fluence irradiation (cf. Fig. 4). A system whose pressure is at the Torr level can have helpful collisional relaxation to begin with, and when it is excited with a high fluence the excitation bottleneck is partially removed. Therefore, under such circumstances, the beneficial role of argon can only be marginal when compared with low fluence experiments.
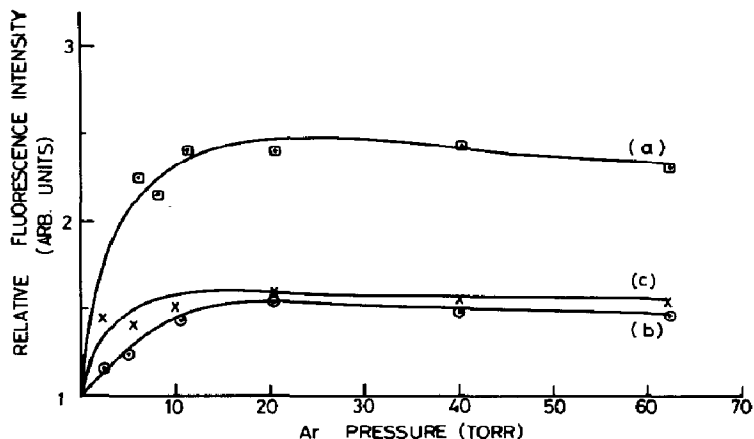
Fig. 4. Addition of argon. Relative intensities of (a) CDF_3^* at $\phi_f = 1$ J cm^{-2}, (b) CDF_3^* at $\phi_f = 95$ J cm^{-2} and (c) DF^* at $\phi_f = 95$ J cm^{-2}.

The temporal behaviour of CDF_3^* emission at $\phi_f = 95$ J cm^{-2} in the presence of argon seems to be single exponential (cf. Fig. 5(a)). Although careful analysis of the data can still resolve a bimodal decay pattern, we do not attach much importance to the faster decay with $\tau_d = 2$ μs. The overall single decay with the typical value $\tau_d = 5 \pm 1$ μs reflects the suppression of the second slow component observed in neat CDF_3. This is due to efficient collisional deactivation of the excited absorber near and below the dissociation threshold by the buffer gas argon. Thus, real time investigation of the CDF_3^* emission substantiates the mechanism invoked earlier for the static cell photolysis experiments wherein selectivity improvement in the MPD of CDF_3–CHF_3 mixture was obtained for argon addition [10,13]. The addition of argon to the mixture results (a) in enhanced energy absorption by CDF_3 because of rotational hole filling and, as a consequence, a higher value for the unimolecular reaction rate and (b) in additional quenching of both CDF_3^* and CHF_3^* (by collisions with the argon). Processes (a) and (b) have the opposite effect on the net accumulation of vibrational energy in CDF_3; process (b) is detrimental to CHF_3^* decomposition. It is therefore possible to choose an optimum buffer gas pressure to increase the relative rate of CDF_3 decomposition over that of CHF_3 and obtain better selectivity.

The slope of the semilogarithmic plot of CDF_3^* intensity vs. time yielded an apparent first-order rate constant for the collisional deactivation process. A plot of this rate constant as a function of buffer gas pressure would have a slope equal to the true bimolecular rate constant of the process. Analysis of the experimental data indicated that the apparent first-order rate constants decreased with argon pressure with a slope of 1.3×10^3 s^{-1} Torr^{-1}.

The emission due to DF^* showed single-exponential decay behaviour with $\tau_d = 3 \pm 1$ μs (cf. Fig. 5(b)), which remained almost invariant with argon pressure. A deactivation rate analysis similar to that for CDF_3^* was not possible because of the instrumental response time limitation.
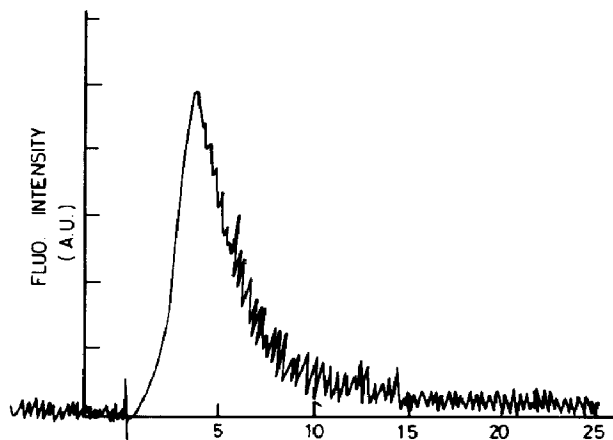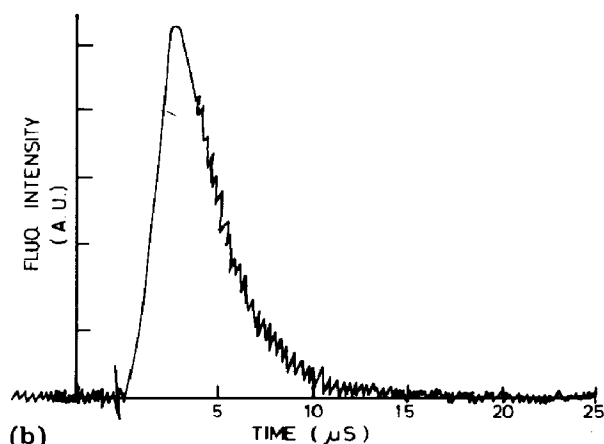
Fig. 5. Emission profiles of (a) CDF_3^* and (b) DF^*, at $\phi_f = 95$ J cm^{-2} and $P(Ar) = 41$ Torr.

3.4. Isotopic selectivity

When a 1:1 mixture of CDF_3 and CHF_3 at various pressures was irradiated with the 10 R(10) CO_2 laser line at a fluence of 70 - 95 J cm^{-2}, IR emission was observed over the wide wavelength region of 2 - 5 μm. The emission was characterized as originating from four species [8]. The emission of vibrationally excited HF^* (2.2 - 3.2 μm) consisted of two peaks, one at 2.4 μm corresponding mainly to the R branch of the $v = 0 \rightarrow 1$ transition, while that at 2.8 μm included several transitions of $\Delta v = 1$ from various higher vibrational levels. CHF_3^* showed emission due to the C—H stretching mode around 3.3 μm, while DF^* and CDF_3^* gave fluorescence around 3.8 μm and 4.4 μm respectively.

The emission of CHF_3^* and HF^* clearly indicates that collisional V—V energy transfer takes place in the mixture whereby non-resonant CHF_3 molecules become excited and dissociate. The isotopic scrambling is the

result of such energy transfer processes. The selectivity in the IR MPD process usually decreases with increasing substrate pressure [19], primarily because of vibrational energy transfer between resonantly excited and off-resonant molecules. Therefore, the isotopic selectivity in the mixture given by the ratio I_{DF^*}/I_{HF^*}, where I stands for the peak intensity of the emission of the respective species, was studied as a function of mixture pressure and laser fluence. Table 1 gives the results obtained under our experimental conditions. In the pressure range 4 - 20 Torr, the selectivity decreased with system pressure. The higher fluence irradiation yielded a lower selectivity, with the substrate pressure having little effect. This is due to collisional energy transfer between highly excited CDF_3^* and CHF_3^* at the high fluence producing a higher yield of HF.

In conclusion, we have monitored time-resolved IR fluorescence from both the reactant and the product in the IR MPD of CDF_3. The effect of argon addition on MPE/MPD in the system was seen in terms of both IRF intensities and time profiles. The suppression of slower components for both CDF_3^* and DF^* indicated that argon effectively quenched the energy transfer processes occurring through collisions. Such processes are expected to minimize isotopic scrambling in the MPD of CDF_3–CHF_3 mixtures. The *in situ* selectivity factor was determined from the ratio of the intensities of DF^* and HF^* for 1:1 CDF_3–CHF_3 mixtures in the pressure range 4 - 20 Torr. This *in situ* information on selective excitation and isotopic scrambling processes can be utilized to devise conditions for improving the MPD yield and selectivity.

TABLE 1

In situ isotopic selectivities in the MPD of 1:1 CDF_3–CHF_3 mixtures

Run	P(total) (Torr)	Selectivity factor S	
		$\phi_f = 70$ J cm^{-2}	$\phi_f = 95$ J cm^{-2}
1	4.2	4.5	—
2	6.2	4.2	2.8
3	10.0	4.0	2.6
4	15.3	3.0	2.5
5	20.0	2.4	—

References

1 A. Ruoff, H. Burger and S. Biedermann, *Spectrochim. Acta, Part A*, 27 (1971) 1359.
2 I. P. Herman and J. B. Marling, *J. Chem. Phys.*, 72 (1980) 516.

3 S. A. Tuccio and A. Hartford, Jr., *Chem. Phys. Lett.*, *65* (1979) 234.
4 I. P. Herman and J. B. Marling, *Chem. Phys. Lett.*, *64* (1979) 75.
5 E. Tschuikow-Roux and J. E. Marte, *J. Chem. Phys.*, *42* (1965) 2049.
6 D. R. Stull and H. Prophet (eds.), *JANAF Thermochemical Tables, U.S. Natl. Bur. Std. NSRDS-NBS 37*, 1971, 2nd edn.
7 S. F. Politanskii and V. U. Shevchuk, *Kinet. Katal.*, *9* (1968) 496.
8 Y. Ishikawa, S. Arai, H. Yamazaki and Y. Hama, *Appl. Phys. B*, *32* (1983) 85.
9 D. K. Evans, R. D. McAlpine and H. M. Adams, *J. Chem. Phys.*, *77* (1982) 3551.
10 V. Parthasarathy, S. K. Sarkar, K. V. S. Rama Rao and J. P. Mittal, *Appl. Phys. B*, *39* (1986) 187.
11 Y. Ishikawa, R. Nakane and S. Arai, *Appl. Phys.*, *25* (1981) 1.
12 J. B. Marling, I. P. Herman and S. J. Thomas, *J. Chem. Phys.*, *72* (1980) 5603.
13 V. Parthasarathy, S. K. Sarkar, K. V. S. Rama Rao and J. P. Mittal, *J. Photochem.*, *29* (1985) 333.
14 C. R. Quick, Jr., and C. Wittig, *J. Chem. Phys.*, *72* (1980) 1694.
15 J. M. Zellweger, T. C. Brown and J. R. Barker, *J. Chem. Phys.*, *83* (1985) 6261.
16 Y. Ishikawa and S. Arai, *Bull. Chem. Soc. Jpn.*, *57* (1984) 2040.
17 P. N. Clough, J. C. Polanyi and R. T. Taguchi, *Can. J. Chem.*, *48* (1970) 2912.
18 M. J. Berry, *J. Chem. Phys.*, *61* (1974) 3114.
19 R. V. Ambartzumian and V. S. Letokhov, in C. B. Moore (ed.), *Chemical and Biochemical Applications of Lasers*, Vol. 3, Academic Press, New York, 1977, Chapter 2, p. 271.