

## Laser Isotope Separation of $^{13}\text{C}$ : A Comparative Study

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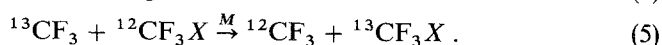
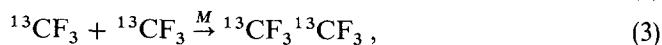
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**Abstract.** IR laser chemistry of  $(\text{CF}_3\text{Br}/\text{Cl}_2)$  mixture and neat  $\text{CF}_2\text{HCl}$  are examined in the context of  $^{13}\text{C}$  enrichment. Decomposition extent, enrichment factor and energy absorbed are measured for both systems at their respective optimum conditions. A direct comparison is obtained by keeping extraneous factors such as laser, its pulse duration, cell, irradiation geometry *etc.* the same. The halogen scavenged  $\text{CF}_3\text{Br}$  MPD requires lower fluence compared to neat  $\text{CF}_2\text{HCl}$  irradiation. Overall throughput for a product with 60–65%  $^{13}\text{C}$  content in a single stage is the same for both systems requiring a similar amount of energy. However, at lower enrichment levels,  $\text{CF}_2\text{HCl}$  MPD is better than  $(\text{CF}_3\text{Br}/\text{Cl}_2)$  photolysis in terms of both product yield and energy absorption.

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IR laser chemistry of carbon compounds has been extensively studied for a long time. A large number of halogenated molecules, mostly methanes, have been subjected to isotope selective, *infrared* multiple photon dissociation (IR MPD) ([1–5] and references therein). Among these,  $\text{CF}_3\text{X}$  ( $\text{X} = \text{I}, \text{Br}, \text{Cl}$ ) and  $\text{CF}_2\text{HCl}$  are quite promising for carbon-13 laser isotope separation (LIS).

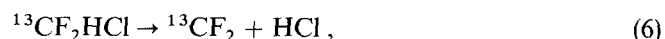
Under selective excitation,  $\text{CF}_3\text{X}$  has the following chemistry [6, 7]:



In general,  $\text{CF}_3\text{X}$  MPD has good selectivity at low pressure and temperature [6–9]. In the above scheme, (2) represents the recombination of the dissociated fragments and limits the decomposition extent. However, judicious addition of a suitable scavenger can minimize the recombi-

nation problem [9]. A number of scavengers have been employed for  $\text{CF}_3\text{X}$  MPD. These include HI, NO,  $\text{O}_2$ ,  $\text{Br}_2$ ,  $\text{Cl}_2$ , and metallic silver (see [5] for individual references). It has been demonstrated that  $^{13}\text{C}$  can be enriched to 97% by a two stage process [10, 11]. It is based on IR MPD of natural  $\text{CF}_3\text{Br}/\text{Cl}_2$  in stage 1 and that of enriched  $\text{CF}_3\text{Cl}/\text{Br}_2$  in stage 2.

For  $\text{CF}_2\text{HCl}$ , laser chemistry on selective excitation is as follows [12]:



$\text{CF}_2\text{HCl}$  MPD is possible even at fairly high pressures ( $\sim 133$  mbar) yielding  $\text{C}_2\text{F}_4$  with 50%  $^{13}\text{C}$  [12, 13]. At lower substrate pressures, two-frequency MPD has yielded a much higher enrichment [14, 15]. However,  $\text{C}_2\text{F}_4$  poses difficulties in closing the chemical cycle for higher enrichment in the second stage.

In laser chemistry, intercomparison of results for two different systems is often difficult especially when reported by different laboratories. Sometimes this is due to non-uniformity in the presentation of results. Moreover, experimental data become convoluted by extraneous factors such as laser type, its pulse duration, photolysis cell, irradiation geometry *etc.* In the present study, we have carried out IR MPD of neat  $\text{CF}_2\text{HCl}$  and  $(\text{CF}_3\text{Br}/\text{Cl}_2)$  mixture for LIS of  $^{13}\text{C}$  keeping the above parameters the same. This has enabled us to obtain a direct comparison between the two systems regarding overall product throughput at a certain  $^{13}\text{C}$  enrichment and the energy expended.

### 1 Experimental

All parametric studies were done in a 1 m long Pyrex cell (volume = 1200 cm<sup>3</sup>) fitted with  $\text{BaF}_2$  windows. A line tunable, TEA  $\text{CO}_2$  laser (Lumonics 103-2) was used without  $\text{N}_2$  in the laser gas mixture for photolysis runs. The laser pulse consisted of a 100 ns FWHM spike without any tail as monitored by a photon drag detector (Rofin 7415).

The beam was folded by a copper mirror and focussed by a BaF<sub>2</sub> lens. The beam waist was located at the cell centre which was 130 cm from the lens. Energy absorption measurement was done by the transmission technique using two calibrated pyroelectric joule meters (Gen Tec ED 500) and a BaF<sub>2</sub> beam splitter. The output of the detectors were fed to a signal averager (Nicolet 1170) and each measurement was averaged for 8 laser shots.

Commercial samples of CF<sub>3</sub>Br (British Oxygen, purity > 99%), CF<sub>2</sub>HCl (PCR Research Chemicals, purity > 99%) and Cl<sub>2</sub> (Air Products, purity 99.5%) were used after several freeze-pump-thaw cycles. Sample pressure was measured by a strain gauge (Leybold MI 200). The atom fraction ratio (<sup>13</sup>C/<sup>12</sup>C) was measured for various species like CF<sub>3</sub>Cl, CF<sub>3</sub>Br and C<sub>2</sub>F<sub>4</sub> by mass spectrometry (VG Micromass 7070F) with a precision of ±1%. In the CF<sub>3</sub>Br/Cl<sub>2</sub> system, Cl<sub>2</sub> was removed from the photolysed sample before mass spectral analysis by cryogenic distillation using *n*-pentane slush at -130°C. Signals were monitored at *m/e* = 132, 131, 130, and 129 for (CF<sub>2</sub>Br)<sup>+</sup> ions to obtain the extent of decomposition in <sup>13</sup>CF<sub>3</sub>Br relative to an unirradiated reference sample. For the CF<sub>3</sub>Cl product, signals were measured at *m/e* = 88, 87, 86, and 85 corresponding to (CF<sub>2</sub>Cl)<sup>+</sup> ions. The enrichment factor β<sub>CF<sub>3</sub>Cl</sub> is defined as

$$\beta_{CF_3Cl} = [(I_{86} + I_{88}) / (I_{85} + I_{87})] ({}^{12}C/{}^{13}C)_{\text{natural}}, \quad (8)$$

where *I<sub>n</sub>* corresponds to the peak height at *m/e* = *n*.

In CF<sub>2</sub>HCl photolysis, the quantity of C<sub>2</sub>F<sub>4</sub> produced was determined by gas chromatography (Shimadzu GC-R1A). A 2 m long, 1.5 mm inside diameter stainless steel column packed with 100–120 mesh Porapak Q was employed isothermally at 100°C with thermal conductivity detection. Helium was used as carrier gas at a flow rate of 50 ml min<sup>-1</sup>. Under these conditions, C<sub>2</sub>F<sub>4</sub> and CF<sub>2</sub>HCl had respective retention times of 2.7 min and 4.3 min. Quantitative analysis was standardized by taking synthetic samples under comparable conditions. The (<sup>13</sup>C/<sup>12</sup>C) ratio in C<sub>2</sub>F<sub>4</sub> was obtained from peaks at 83, 82 and 81 of (C<sub>2</sub>F<sub>3</sub>)<sup>+</sup> ions. Combining the GC data with isotopic distribution in C<sub>2</sub>F<sub>4</sub>, the extent of decomposition in <sup>13</sup>CF<sub>2</sub>HCl and <sup>12</sup>CF<sub>2</sub>HCl was found out. The enrichment factor for C<sub>2</sub>F<sub>4</sub> is defined as:

$$\beta_{C_2F_4} = [(2I_{83} + I_{82}) / (2I_{81} + I_{82})] ({}^{12}C/{}^{13}C)_{\text{natural}}. \quad (9)$$

The reaction volume per pulse *V<sub>R</sub>* is given by

$$V_R = Y V_{\text{beam}}, \quad (10)$$

where *Y* is given by the expression

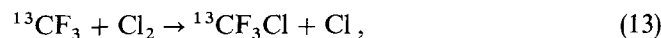
$$Y = [1 - (N/N_0)^{1/n}] (V_{\text{cell}}/V_{\text{beam}}). \quad (11)$$

In (11), *N<sub>0</sub>* and *N* represent the number of <sup>13</sup>C reactants before and after irradiation with *n* pulses, respectively. The product of partial pressure of <sup>13</sup>C species and *V<sub>R</sub>* can be expressed as mbar cm<sup>3</sup> (or mole, or gm *etc.*) pulse<sup>-1</sup>. This corresponds to the throughput of the LIS process. For the comparative study, photolysis conditions such as substrate/scavenger pressure, composition, wavenumber, focal fluence were chosen from the results of parametric studies carried out in our laboratory as well as those reported in [5, 10, 12, 13].

## 2 Results and Discussion

### 2.1 IR MPD of (CF<sub>3</sub>Br/Cl<sub>2</sub>)

Selective excitation of <sup>13</sup>CF<sub>3</sub>Br in the presence of Cl<sub>2</sub> gives rise to the following laser chemistry:



<sup>12</sup>CF<sub>3</sub>Cl could also be formed depending on the system's selectivity. Figure 1 shows the results obtained for (CF<sub>3</sub>Br/Cl<sub>2</sub>) photolysis. For irradiations at 1035.5 cm<sup>-1</sup> [9 P(32)] and 1033.5 cm<sup>-1</sup> [9 P(34)], *V<sub>R</sub>* and β showed a sharp dependence on the focal fluence φ, but in a mutually opposing way. Typically, operating at 3 J cm<sup>-2</sup>, it was possible to obtain the product with ≈ 1:1 composition for <sup>13</sup>C: <sup>12</sup>C with moderate throughput for 9 P(34) photolysis.

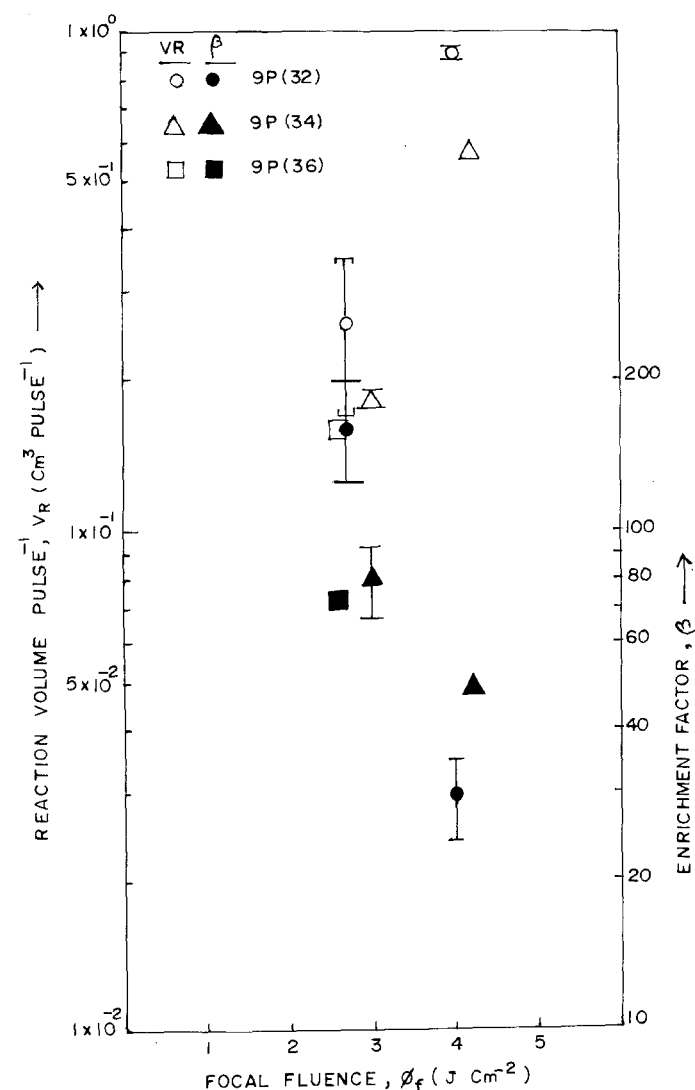


Fig. 1. (CF<sub>3</sub>Br/Cl<sub>2</sub>) MPD. *V<sub>R</sub>* (○, △, □) and β<sub>CF<sub>3</sub>Cl</sub> (●, ▲, ■) as a function of fluence for the lines 9 P(32), 9 P(34) and 9 P(36). Total pressure for 1:4 (CF<sub>3</sub>Br/Cl<sub>2</sub>) = 66.5 mbar

2.2 Neat  $\text{CF}_2\text{HCl}$  Photolysis

Laser chemistry of neat  $\text{CF}_2\text{HCl}$  is as per reactions (6) and (7).  $\text{C}_2\text{F}_4$  produced had a distribution of  $^{13}\text{CF}_2^{12}\text{CF}_2$  and  $^{12}\text{CF}_2^{12}\text{CF}_2$  as well in addition to  $^{13}\text{CF}_2^{13}\text{CF}_2$  due to dissociation of  $^{12}\text{CF}_2\text{HCl}$  governed by the system's selectivity. Runs were made for both 66.5 and 133 mbar neat  $\text{CF}_2\text{HCl}$ . Irradiations were done at  $1046.8\text{ cm}^{-1}$  [9 P (20)] and  $1045.0\text{ cm}^{-1}$  [9 P (22)] as a function of  $\phi$ . For both 9 P (20) and 9 P (22),  $V_R$  and  $\beta$  were found to be sensitive to  $\phi$  (cf. Fig. 2). However, at a given  $\phi$  and  $\text{CF}_2\text{HCl}$  pressure, 9 P (20) gave better  $V_R$  but lower  $\beta$  compared to respective values for 9 P (22) run. For a given  $\phi$ , photolysis of 133 mbar  $\text{CF}_2\text{HCl}$  by 9 P (20) gave a better value for  $\beta$  compared to that at 66.5 mbar, but followed a reverse trend for  $V_R$ . The same trend was observed for 9 P (22) irradiation. These observations agreed with the trend reported in the literature [12].

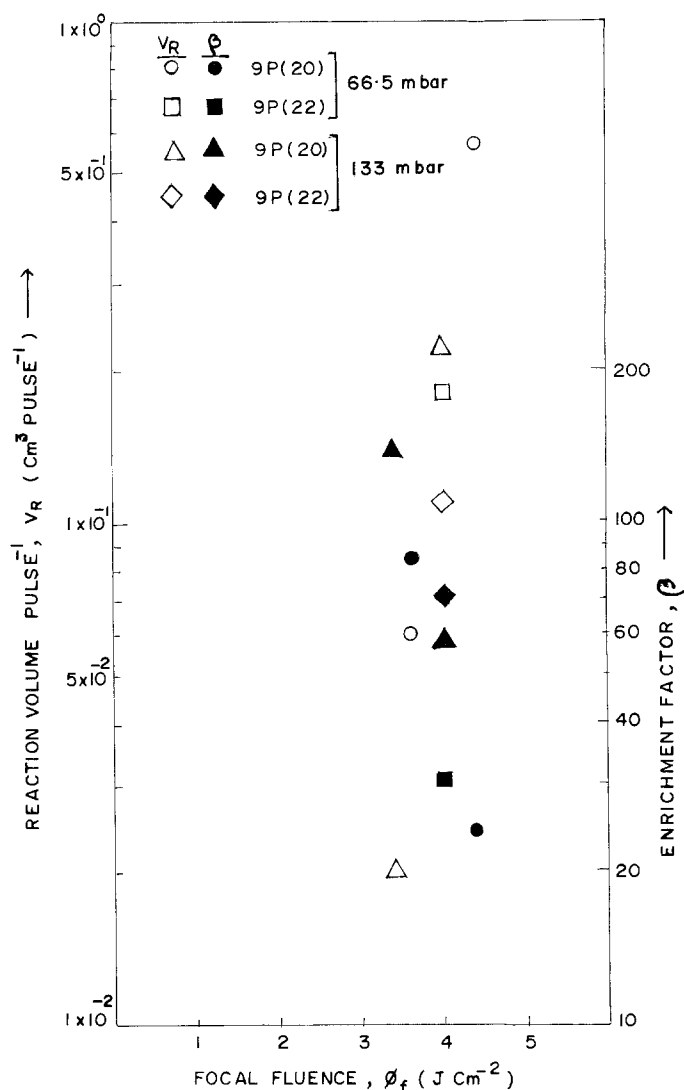


Fig. 2. Neat  $\text{CF}_2\text{HCl}$  MPD.  $V_R$  (○, □, △, ◇) and  $\beta_{\text{C}_2\text{F}_4}$  (●, ■, ▲, ◆) as a function of pressure and focal fluence for 9 P (20) and 9 P (22) lines for 66.5 and 133 mbar  $\text{CF}_2\text{HCl}$

2.3 Intercomparison between  $(\text{CF}_3\text{Br}/\text{Cl}_2)$  and  $\text{CF}_2\text{HCl}$  Systems

The threshold energy for C–Br bond cleavage in neat  $\text{CF}_3\text{Br}$  is  $288\text{ kJ mole}^{-1}$  [16]. In two-centre atomic eliminations, like  $\text{CF}_3\text{–Br}$  MPD, the energy required for dissociation is roughly the same as the reaction endoergicity. There is virtually no barrier for the back reaction, viz., recombination between  $\text{CF}_3$  and Br radicals. However, for a three-centre molecular elimination in  $\text{CF}_2\text{HCl}$ , the energy threshold for dissociation can be higher than the reaction endoergicity. The overall threshold for  $\text{CF}_2\text{HCl}$  dissociation,  $226\text{ kJ mole}^{-1}$ , is given by the reaction endoergicity ( $201\text{ kJ mole}^{-1}$ ) plus the energy barrier for recombination between  $\text{CF}_2$  and  $\text{HCl}$  ( $25\text{ kJ mole}^{-1}$ ) [17]. These energy considerations suggest that neat  $\text{CF}_2\text{HCl}$  MPD would require a lower fluence compared to the neat  $\text{CF}_3\text{Br}$  case and it has been experimentally verified. [7, 8, 12]. However, our results indicate (cf. Figs. 1, 2) that IR laser chemistry of  $(\text{CF}_3\text{Br}/\text{Cl}_2)$  requires lower  $\phi$  relative to that for neat  $\text{CF}_2\text{HCl}$  for attaining a certain combination of  $V_R$  and  $\beta$ . Therefore, it appears that  $\text{Cl}_2$  scavenges  $\text{CF}_3$  radicals quite well and reduces the recombination between  $\text{CF}_3$  and Br in the mixture following MPD. Reaction (2) is very facile for neat  $\text{CF}_3\text{Br}$  MPD resulting in poor decomposition and high fluence requirement. When recombination effects are minimized in  $\text{CF}_3\text{Br}$  MPD with a scavenger, the rates of reactions (13) and (7) govern the overall throughput in  $(\text{CF}_3\text{Br}/\text{Cl}_2)$  and  $\text{CF}_2\text{HCl}$  systems, respectively.

From our results in Figs. 1, 2, we can compare the two systems for different levels of enrichment. Photolysis of 1:4  $(\text{CF}_3\text{Br}/\text{Cl}_2)$  mixture at 66.5 mbar total pressure by 9 P (32) at  $\phi = 2.7\text{ J cm}^{-2}$  gave  $V_R = 0.26\text{ cm}^3 \text{ pulse}^{-1}$  and  $\beta = 162$ . In comparison, the corresponding values of  $V_R$  and  $\beta$  in the photolysis of 133 mbar  $\text{CF}_2\text{HCl}$  by 9 P (20) at  $\phi = 3.4\text{ J cm}^{-2}$  were 0.02 and 141, respectively. Although  $\text{CF}_2\text{HCl}$  pressure is ten times that of  $\text{CF}_3\text{Br}$ ,  $V_R$  is lower by more than one order of magnitude. Thus both the systems tend to give a similar throughput for enriched product with a  $^{13}\text{C}$  content of 60–65%. But if one is interested in a product with 50%  $^{13}\text{C}$  content,  $\beta$  needs to be around 89. In this case,  $(\text{CF}_3\text{Br}/\text{Cl}_2)$  MPD gives three times better  $V_R$  values compared to  $\text{CF}_2\text{HCl}$ . However, as the operating pressure in  $\text{CF}_2\text{HCl}$  is ten times that of  $\text{CF}_3\text{Br}$ , the  $\text{CF}_2\text{HCl}$  system is better by a net factor of three in terms of throughput than the halogen scavenged  $\text{CF}_3\text{Br}$  system.

Figures 3, 4 show the dependence of fractional energy absorption as a function of scavenger pressure in the 13.3 mbar  $\text{CF}_3\text{Br}$  case and of the substrate pressure in the neat  $\text{CF}_2\text{HCl}$  case, respectively, for different focal fluence. Addition of  $\text{Cl}_2$  has a dual promotional role in  $\text{CF}_3\text{Br}$  MPD. It increases the multiple photon absorption in  $\text{CF}_3\text{Br}$  through the rotational hole filling mechanism as seen in Fig. 3. At the same time, it enhances  $\text{CF}_3\text{Br}$  MPD yield by scavenging the  $\text{CF}_3$  radicals effectively. At lower  $\text{Cl}_2$  pressures,  $\leq 30$  mbar, the fractional energy absorption increases with fluence for a particular composition. However, the effect is diminished at higher  $\text{Cl}_2$  pressures. Figure 3 also shows that for pulses with a  $1\text{ }\mu\text{s}$  tail, collisional processes induce higher energy deposition into the system

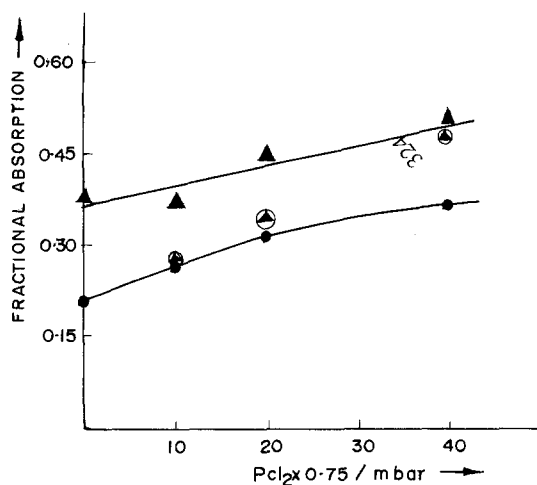


Fig. 3. Fractional energy absorption in  $(\text{CF}_3\text{Br}/\text{Cl}_2)$  as a function of  $\text{Cl}_2$  pressure and focal fluence  $p_{\text{CF}_3\text{Br}} = 13.3$  mbar, 9 P (32) line, ●  $2.5 \text{ J cm}^{-2}$ , 100 ns FWHM pulse, ○  $2.5 \text{ J cm}^{-2}$ , pulse with  $1 \mu\text{s}$  tail, ▲  $3.7 \text{ J cm}^{-2}$ , pulse with  $1 \mu\text{s}$  tail

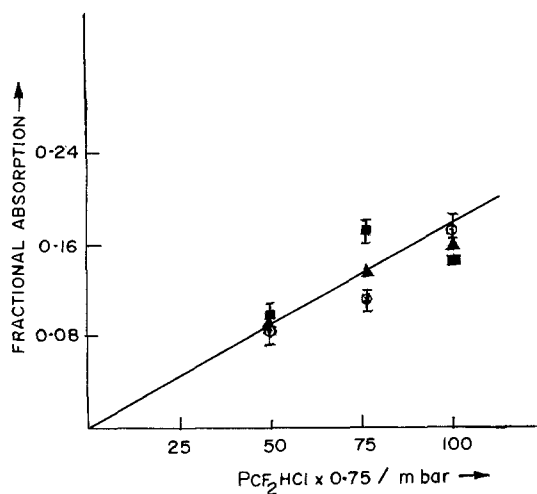


Fig. 4. Fractional energy absorption in neat  $\text{CF}_2\text{HCl}$  as a function of substrate pressure and fluence; 9 P (20) line, 100 ns FWHM pulse, ■  $1.9 \text{ J cm}^{-2}$ , ○  $3.0 \text{ J cm}^{-2}$ , ▲  $4 \text{ J cm}^{-2}$

compared to excitation with 100 ns FWHM pulses at the same  $\phi$ . For neat  $\text{CF}_2\text{HCl}$ , the fractional energy absorption is almost invariant with fluence (*cf.* Fig. 4). The absolute energy absorbed by  $\text{CF}_3\text{Br}/\text{Cl}_2$  system compared to neat  $\text{CF}_2\text{HCl}$  is several times higher and this will have a bearing on the economics of the chosen process.

Table 1 gives comparative data for both neat  $\text{CF}_2\text{HCl}$  and  $\text{CF}_3\text{Br}/\text{Cl}_2$  systems MPD in terms of absolute product quantity per pulse, %  $^{13}\text{C}$  content and  $\epsilon$ , the photon energy expenditure in keV per separated C atom for laser chemistry. We employed a converging beam rather than a uniform one of constant fluence and our  $\epsilon$  values tend to be on the higher side as compared to those reported in [12]. This is due to inclusion of energy losses in the low intensity regions.

It can be noted that for obtaining a certain quantity of product with about 60%  $^{13}\text{C}$  both processes have comparable energy requirement. However, at a lower  $^{13}\text{C}$  content,  $\text{CF}_2\text{HCl}$  MPD scores over the  $(\text{CF}_3\text{Br}/\text{Cl}_2)$  system both in terms of product quantity and  $\epsilon$  values. For example, for 25–40%  $^{13}\text{C}$ , there is nearly a two–three times better throughput and ten times energy advantage for the former case relative to the latter one. However, the attractive point in the case of  $\text{CF}_3\text{Br}/\text{Cl}_2$  is that the end product  $\text{CF}_3\text{Cl}$  can be readily converted into  $\text{CF}_3\text{Br}$  with  $^{13}\text{C} \geq 95\%$  in stage 2 of the photolysis involving  $\text{Br}_2$  [11]. For the neat  $\text{CF}_2\text{HCl}$  system, this aspect may pose some problems because “closing the chemical cycle” with  $\text{C}_2\text{F}_4$  for further upgrading the enrichment is not straightforward. Nevertheless, chemical conversion of  $\text{C}_2\text{F}_4$  into CO and employing it in cryogenic distillation may overcome this problem. Recently, it has been shown that by innovative choice of a scavenger, it is possible to obtain  $\geq 90\%$  enrichment by a 2-stage approach using the  $\text{CF}_2\text{HCl}/\text{Br}_2$  or  $\text{CF}_2\text{HCl}/\text{HI}$  MPD route [18, 19]. The  $\text{CF}_2\text{HCl}/\text{HI}$  system is particularly noteworthy because the stage 1 product, *viz.*,  $\text{CF}_2\text{HI}$  directly undergoes MPD at the same wavenumber like its precursor and gives rise to high enrichment.

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Table 1. Comparative results of  $\text{CF}_2\text{HCl}$  and  $\text{CF}_3\text{Br}/\text{Cl}_2$  systems in terms of throughput, enrichment and energy expenditure

System <sup>a</sup>	Total pressure [mbar]	Focal fluence [ $\text{J cm}^{-2}$ ]	% $^{13}\text{C}$ in the product	$^{13}\text{C}$ separated per pulse [ $10^{-10}$ kg]	$\epsilon$ keV per C atom
Neat $\text{CF}_2\text{HCl}$	66.5	3.6	49	0.23	0.287
—	66.5	4.4	21	2.13	0.016
—	133.0	3.4	61	0.16	1.07
—	133.0	4.0	39	1.71	0.073
1:4 $\text{CF}_3\text{Br}/\text{Cl}_2$	66.5	2.7	65	0.20	1.3
—	66.5	3.5	30	0.35	0.72
—	66.5	4.0	25	0.69	0.21

<sup>a</sup> Tail free, 100 ns FWHM laser pulses were used for all the runs. 9 P (20) line for neat  $\text{CF}_2\text{HCl}$  MPD and 9 P (32) line for  $\text{CF}_3\text{Br}/\text{Cl}_2$  mixture MPD were employed

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