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Laser enrichment of carbon-13: operational experience with a large photochemical reactor for macroscopic separation

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Abstract

This paper describes the operational experience of carrying out the carbon-13 enrichment by infrared multiple photon dissociation of natural CF_2HCl in a 280 l volume photochemical reactor (PCR) by a batch process. The modular type PCR employs a multi pass refocusing Herriott optics for efficient photon utilization and has an independent gas blower arrangement for gas circulation in each of the three modules during laser photolysis. We could typically obtain a production rate of about 5 mg/h. for total carbon with a ^{13}C isotopic purity of ~40%.

Keywords: Laser enrichment; Photochemical reactor; Carbon isotopes; IR MPD

1. Introduction

Among the eight isotopes the element carbon has, ranging from C-9 to C-16, those with stable nuclei, viz., C-12 and C-13 have many important applications. The minor isotope C-13 with a natural abundance of 1.1% is a valuable tracer in chemical, biological and environmental science [1–3]. A number of C-13 labeled compounds like urea, glucose, fructose, triolein are extremely useful in the medical diagnostic investigation of various body organs. In these, the compound, fed orally to a patient, undergoes metabolism giving rise to CO_2 which is collected from the exhaled breath for isotopic analysis. By measuring the C-13 to C-12 ratio of the collected sample, the health condition of the organ can be readily evaluated. For example, using C-13 urea, an early detection of *Helicobacter Pylori* is possible [4]. This organism is responsible for the stomach ulcer which when not detected may lead to stomach cancer. By using $^{13}CO_2$, $^{13}CH_3OH$ and $^{13}CF_3Br$ as working media, isotopically labeled gas lasers are possible.

When a C-13 enrichment campaign is carried out, the residual material becomes progressively richer in C-12. For example, when 99% of the initial C-13 is removed, the C-12 atom percentage rises to 99.99. Pure C-12 has interesting applications in materials science and technology. It has been shown that a synthetic diamond crystal made from highly enriched C-12 has 50% better thermal conductivity than that of the best quality natural diamond containing 1.1% of C-13 [5]. Such material has potential uses as heat sink in microelectronics. Further, solvents enriched in C-12 find applications in NMR spectroscopy.

The emerging market for medical applications of C-13 is projected to be in the range of 100s of kg per year [6]. The current world production of C-13 at 99% concentration is only a few 10s of kg and is based on the cryogenic distillation of carbon monoxide [7]. Since the elementary stage separation factor is extremely low, a very large number of stages are needed and the equilibration time takes several months. Further, the process is quite capital intensive.

Laser isotope separation (LIS) by infrared laser chemistry of polyatomic molecules has made a lot of progress and the last two decades have seen considerable efforts for the isotopes of light elements like carbon, oxygen and silicon [8–12]. The achievement is quite significant especially for carbon isotopes' separation wherein macroscopic operating scales have been realized [13–16].

Our investigations of the IR laser chemistry of two promising systems, viz. (1) neat CF_2HCl and (2) CF_3Br/Cl_2 containing 1.1% C-13 using a 0.5 W pulsed CO_2 laser have

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identified the parametric conditions for optimum dissociation yield and selectivity [17,18]. Further, in a validation study, the neat CF_2HCl system was reinvestigated using a 10 W laser system and the results obtained were compared with those obtained earlier under identical conditions [19]. Based on the results of these cell experiments with single pass optical arrangement, we extended the study to photolysis in the PCR under multi pass, refocusing optics [20,21]. The validation exercise was found to be very important and helped us anticipate the results in the PCR runs using the 10 W laser.

The current paper gives the details of our efforts for scaling up of the process for carbon-13 enrichment using the PCR and the 10 W laser. It also describes the development of a cryogenic distillation set up and a preparative gas chromatograph for large scale separation/collection of the isotopically enriched photoproduct in the post irradiation stage.

2. Experimental

Fig. 1 gives a general description of our system designed for carrying out the PCR runs. Laser and accessories include the pulsed CO_2 laser source (Macrooptica) and various optical elements like windows, grating, mirrors, lenses etc., also detectors for energy (GenTec) and temporal profile measurements (Edinburgh Instruments). The photochemical reactor (PCR) employs Herriott multipass refocusing (MPRF) optics, has a built in blower in each of the module for gas circulation during the laser irradiation. Pressure monitoring was done by a calibrated Strain gauge (BOC Edwards). Product separator consists of a home-made cryogenic distillation set up and a commercial preparative gas chromatograph (Toshniwal Instruments) for isolating and purifying the enriched photoproduct from the bulk residual reactants and other side products. Diagnostics include an analytical gas chromatograph (Shimadzu), quadrupole mass spectrometer (VG Elemental). Feed incorporates a gas handling system.

2.1. Laser source

The pulsed CO_2 laser tunable over 70 lines in the 9.0–11.0 μm band region was operated on 9 P(22) line at 10 W average power (1 J energy on 9 P(22) line at 1045 cm^{-1} with a repetition rate of 10 Hz). The temporal profile of the emitted pulse could be varied by adjusting the lasing gas mixture (CO_2, N_2 and He) composition.

2.2. Photochemical reactor

The multipurpose PCR made of stainless steel consisted of three identical modules and is suitable for use with different mirror systems of various radii of curvature ranging from 10 to 100 cm depending on the fluence requirement of the laser chemistry process. The laser interaction chamber (LIC) in each module has a length of 50 cm (overall length 150 cm for the PCR with three such modules connected in a linear chain) and a diameter of 30 cm. Each of the LIC module has a transverse blower unit for gas circulation. In each of the gas blower chamber, a centrifugal blower (capacity of 50 m^3/h at 100 Torr pressure) is mounted to facilitate a continuous circulation of the gases in the irradiated zone at variable speeds to avoid thermal effects during irradiation. This arrangement typically provides three times replacement of the sample in the irradiated zone between successive laser pulses at 10 Hz laser repetition rate. In the absence of such a circulation, there could be a severe selectivity loss in the system. The vacuum integrity of the system with gas circulation using the centrifugal blowers has been found to be quite good over long periods of irradiation time. This is very crucial for the successful enrichment run. The blowers were operated for over 100 h initially for testing the reliability.

The Herriott type MPRF optics [22,23] housed in the LIC for efficient photon utilization was a stable optical resonator (cf. Fig. 2) consisting of two coaxial concave mirrors separated by the length of the reactor. The laser beam was injected off axially through a small hole near the periphery of

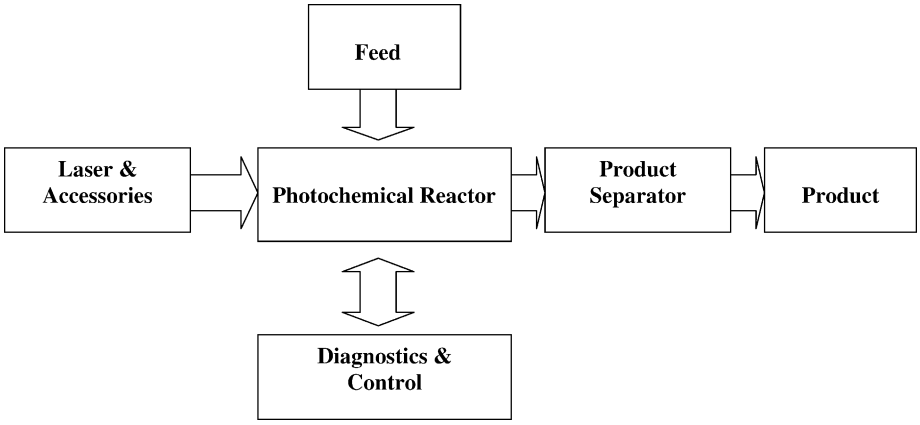

Fig. 1. Block diagram of the general schematic.

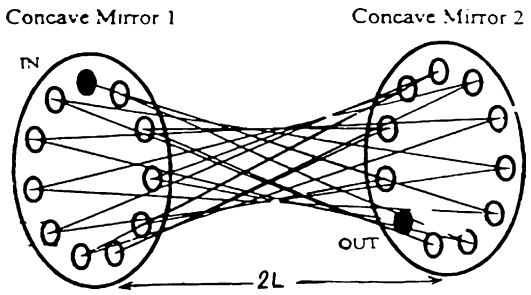

Fig. 2. Herriott multi pass, refocusing optics, 2*L*: inter mirrors' separation distance.

one of the mirrors and traveled between them in a zigzag manner. With proper design and alignment, the beam after every reflection can be refocused to the same waist radius in the central plane between the mirrors. The mirror material and its coating were such that they could withstand the hard irradiation conditions in the chemical environment of the photolysis. For the present system, a pair of large size (15 cm diameter) high reflectivity mirrors (better than 98.5%) was used. Initial alignment of the mirrors was done using a He–Ne laser and final alignment was done with the CO_2 laser. In all the runs, the CO_2 laser made a total of 13 passes between the mirrors.

2.3. Cryogenic distillation system

After the PCR runs, the useful end product needed to be isolated/pre-concentrated from the bulk starting material and other side products in gas phase in the post irradiation stage. For this purpose, a cryogenic distillation apparatus made of glass was developed for the isolation of tetrafluoroethylene (C_2F_4) from chlorodifluoromethane (CF_2HCl). The system had three components, viz., re-boiler (maintained at −40 °C), distillation column, and condenser (maintained at −140 °C). The overall volume of the apparatus was about 5 l.

In this temperature range, the appreciable vapor pressure difference between C_2F_4 and CF_2HCl facilitated the separation of the more volatile C_2F_4 from the residual CF_2HCl. Long term vacuum integrity, good refluxing of the distillate and very good thermal isolation of the distillation assembly from the surroundings were found to be very important for efficient product separation during the distillation process.

2.4. Preparative gas chromatograph

After pre-concentration, final purification of the enriched product was done by the preparative gas chromatograph unit which had a 2.5 m long and 6 mm diameter Porapak-Q column. In a single batch, more than 25 cm^3 of the process mixture at atmospheric pressure can be loaded. The equipment had a custom built sample handling system. Using the combination of a programmable logic controller, auto gas injection valve and a stream selection valve, the process of automatic sampling, injection and separation of the fractions could be conveniently effected. Fig. 3 gives a schematic of the set up.

2.5. Analysis methodology

Fifty Torr commercial grade, natural Freon-22 was used as feed in all the PCR runs. The blowers were operated to provide the gas a linear velocity of 5 m/s in the zone between the mirrors. Samples were periodically drawn from the PCR using a sampling loop for analyses by gas chromatography and mass spectrometry to determine the quantity of the C_2F_4 photoproduct formation and its C-13 content.

The dissociation extent per pulse was expressed in terms of the reaction volume, V_R. The latter was defined as the product of the experimentally measured specific dissociation rate, *d*, for a particular isotopic species and the reactor volume, V_{PCR}.

For example, the reaction volume for C-13 species would be

$$^{13}V_R = d_{13} \times V_{PCR} \quad (1)$$

The term "*d*" was evaluated using the expression:

$$N_m = N_0(1-d)^m \quad (2)$$

where N_m and N_0 corresponded to the number of a particular isotopic species after "*m*" pulses and before the photolysis, respectively.

The isotopic composition for carbon in the photoproduct, C_2F_4 was measured by mass spectrometry using the signal intensities at (*m*/*e*) values of 81, 82 and 83 corresponding to $^{12}CF_2{}^{12}CF^+$, $^{13}CF_2{}^{12}CF^+$ and $^{13}CF_2{}^{13}CF^+$ ions, respectively. From these values, the product enrichment factor, β was calculated to be:

$$\beta = \frac{(2 \times I_{83} + I_{82}) \times 98.89}{(2 \times I_{81} + I_{82}) \times 1.11} \quad (3)$$

Extent of decomposition in $^{13}CF_2HCl$ was obtained from the experimental β values along with the total product yield measured by gas chromatography. The dissociation selectivity, *S*, defined as

$$S = \frac{^{13}V_R}{^{12}V_R} \quad (4)$$

was calculated from the ratio of reaction volume for the respective isotopic species.

3. Laser isotope separation schemes

In the late 1970s, several groups all over the world investigated the IR laser chemistry of trifluorohalomethanes [24–28], CF_3X, where X = I, Br and Cl, using a pulsed carbon-di-oxide laser. The C–F stretching mode of these species has a well resolved isotopic shift of about 25 cm^{-1}

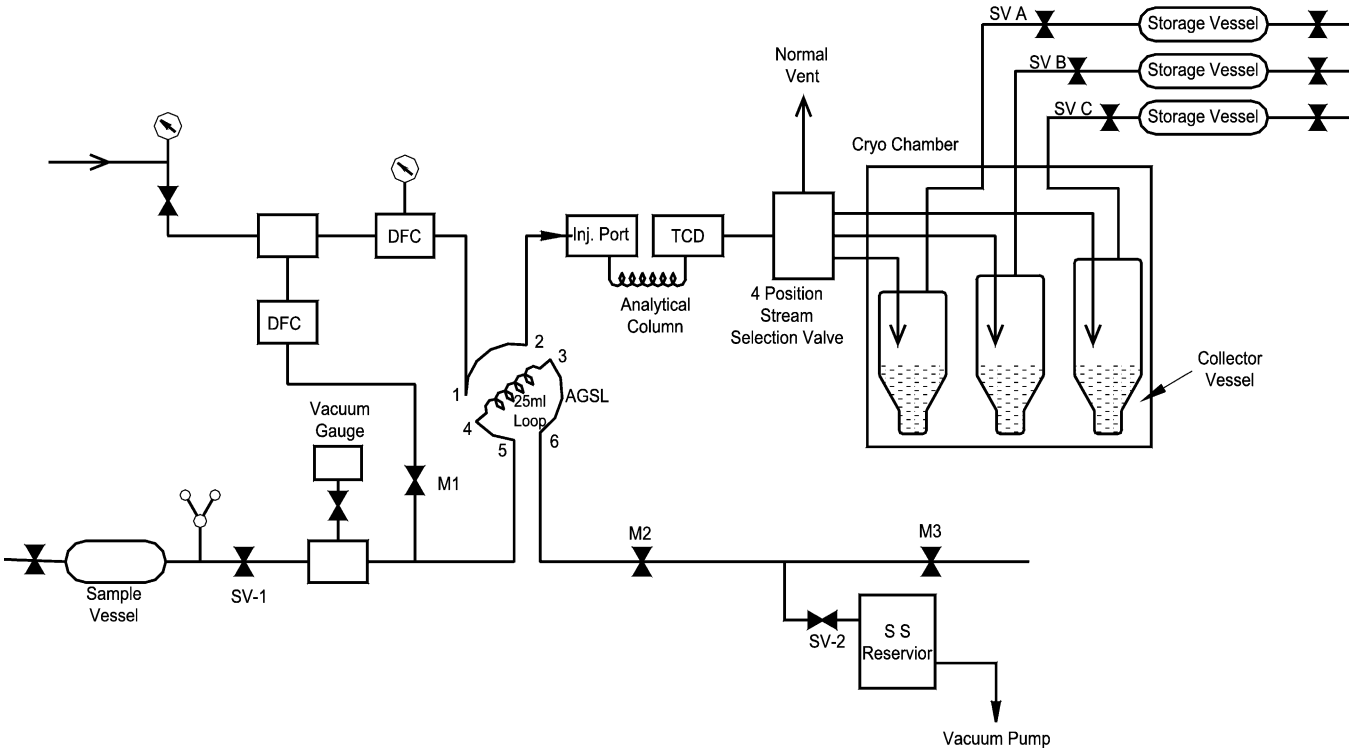

Fig. 3. Schematic of the preparative gas chromatograph. SV-1, SV-2: solenoid valves; M1, M2, M3: manually operated valves; SVA, SVB, SVC: stream selection valve positions; TCD: thermal conductivity detector; DFC: differential flow controller; AGSL: auto gas sampling loop.

for the carbon isotopes and can be readily excited by a tunable, pulsed CO_2 laser.

While the C-13 enrichment in the end product, C_2F_6, was successfully demonstrated at low pressures and low temperature, there were, however, some major disadvantages with this system. Since the rate of formation of the product nearly equaled the rate of recombination of the dissociated fragments, the overall dissociation yield was very low. Operation at higher energy density (fluence) to increase the yield severely degraded the enrichment factor. Also, the product throughput was quite small as the substrate pressure was less than 1 Torr.

Subsequently, two viable schemes were developed. The first one developed at the National Research Council, Canada [8,9], was good for getting 50% enrichment at macroscopic levels. In this, $^{13}CF_2HCl$ at its natural concentration in chlorodifluromethane, underwent IR MPD giving rise to difluorocarbene, CF_2 and hydrogen chloride, HCl. The ultimate end product was tetrafluoroethylene, C_2F_4 with a C-13 atom fraction of 50%.

$$^{13}CF_2HCl \xrightarrow{\text{TEA } CO_2 \text{ laser}} :^{13}CF_2 + HCl \quad (5)$$

$$2 :^{13}CF_2 \rightarrow {}^{13}C_2F_4 \quad (6)$$

Using this system, one can obtain still higher enrichment in a single stage but at the cost of product quantity.

The second one, known as Lausanne–Zurich (L–Z) cyclic scheme [29], made use of a two stage, closed chemical cycle and was very useful for getting high enrichment level. If a product with better than 90% C-13 enrichment was to be obtained in a single stage from the initial 1.1% level, a stringent dissociation selectivity, *S*, better than 800 would be required. Such conditions normally exist only at very low pressures giving rise to very low throughput. In the L–Z scheme, the problem was split into two parts. Stage 1 aimed at a large throughput limiting the enrichment to about 50%. The product from stage 1 was recovered and employed in stage 2 leading to higher enrichment. Following was the IR laser chemistry of L–Z scheme.

3.1. Stage 1

$$\text{Natural } {}^{13}CF_3Br \xrightarrow[Cl_2]{\text{TEA } CO_2 \text{ laser}} \text{enriched } {}^{13}CF_3Cl + Br_2 \quad (S = 90). \quad (7)$$

3.2. Stage 2

$$\text{Enriched } {}^{13}CF_3Cl \xrightarrow[Br_2]{\text{TEA } CO_2 \text{ laser}} \text{highly enriched } {}^{13}CF_3Br + Cl_2 \quad (S = 9). \quad (8)$$

The L–Z scheme, by employing an appropriate halogen scavenger in the first stage, overcame the recombination problem

encountered in the neat CF_3X MPD (vide infra) resulting in better dissociation yield. It also helped in closing the chemical cycle in the first stage to obtain a product which was a suitable starting material in the second stage for further enrichment.

4. Optimization studies

Table 1 summarizes the experimental details of the laboratory scale preparation of the C-13 enriched materials in our laboratory under optimized conditions [17,18]. Using these, laboratory scale quantities of different enriched materials were obtained.

5. Macroscopic scale LIS studies

Fuss et al. [13–15] have demonstrated the large scale separation of both C-13 and C-12 isotopes using a Q-switched CO_2 laser in the isotopically selective photolysis of CF_2HCl and He mixture. For achieving this, they converted an industrial CW CO_2 laser into a mechanically Q-switched system which emitted 250 ns duration pulses of a few mJ energy at 5–10 kHz repetition rate. For the C-13 enrichment, the process involved the irradiation of material at a total pressure of 150 Torr (1:9 CF_2HCl:He mixture) in a circulatory cell for a large number of batches over 2 weeks which ultimately isolated 25 gram of total carbon at 50% C-13 enrichment from an overall processing of about 29 kg. For the C-12 case, 4 moles of chlorodifloromethane was processed in all over a period of 2 weeks to yield CF_2HCl containing a C-12 atom fraction of 99.99%.

In the Russian demonstration facility, Baranov and co-workers [16] have reported a production rate of 100 mg of ^{13}C/h with about 42% C-13 concentration in C_2F_4 using a 1 kW pulsed CO_2 laser operating at 100–1000 Hz repetition rate.

Table 1
Optimum parametric conditions for laboratory scale preparation

C-13 enrichment: 50% (neat CF_2HCl MPD)
Substrate pressure: 100 Torr
Irradiation frequency: 1045 cm^{-1} [9 P(22) line]
100 ns tail-free pulses, focal fluence: 4 J cm^{-2}
Reactor volume: 1 l, reaction volume: 0.4 cc $pulse^{-1}$
Product isolated: C_2F_4 (C-13 content = 50%)
Stage 1: natural CF_3Br/Cl_2 MPD
Total pressure: 50 Torr (1:4 mixture)
Irradiation frequency: 1035.5 cm^{-1} [9 P(32) line]
100 ns tail-free pulses, focal fluence: 3.6 J cm^{-2}
Reactor volume: 20.6 l, reaction volume: 0.55 cc $pulse^{-1}$
Product isolated: CF_3Cl (C-13 content = 50%)
Stage 2: enriched CF_3Cl/Br_2 MPD
Total pressure: 21 Torr (1:6 mixture)
Irradiation frequency: 1057.3 cm^{-1} [9 P(8) line]
100 ns tail-free pulses, focal fluence: 1.7 J cm^{-2}
Reactor volume: 126 cc, reaction volume: 0.022 cc $pulse^{-1}$
Product isolated: CF_3Br (C-13 content > 95%)

5.1. Photolysis runs in the PCR

Before carrying out the runs on the large scale PCR, it was necessary to validate with the 10 W laser our previous results obtained under optimum conditions with a 0.5 W CO_2 laser on the neat CF_2HCl [17]. Such studies for C-13 enrichment carried out with a 10 W pulsed CO_2 laser gave rise to somewhat different results for the conversion compared to those obtained with a 0.5 W laser under identical experimental conditions. Photolysis was done for various incident pulse energies and substrate pressures for the CO_2 laser lines, 9 P(22) and 9 P(26). The results for C-13 decomposition extent and the β values were found to be self consistent and on an expected trend as per our earlier work [17] for a given laser at a particular set of parametric conditions vis a vis substrate pressure, laser line, pulse duration and focal fluence. There was, however, a wide variation in the absolute conversion of C-13 species reacted per pulse in the inter comparison of data obtained with the two lasers. For example, irradiation of 50 Torr sample with the 9 P(22) line with both the lasers gave rise to the photoproduct, C_2F_4 with about 50% carbon-13 content. However, the average $^{13}V_R$ value was about 0.25 cm^3 per pulse for the 0.5 W laser whereas it was about 0.03 cm^3 per pulse for excitation with the 10 W laser under identical irradiation condition. The experimental result was verified a number of times to make sure that there was no extraneous factors involved. A similar trend was observed for the 9 P(26) line also.

Theoretical simulation of the reaction volume for both the cases [19] indicated that the apparent discrepancy was due to a slight difference in the cell windows' absorption for the two lasers, beam waist dimensions and the net resultant fluence gradient the sample was exposed to.

Initial computations took into account a very slight difference in the beam waist dimensions for the two lasers. This, however, could not satisfactorily explain the large difference observed in the experimental results. Subsequently, energy loss at the entrance BaF_2 window was carefully checked for both the lasers. While the average loss with the 0.5 W laser was about 11% at the irradiation frequency, the corresponding value was found to be 3% higher for the 10 W laser. Based on these values, computations were repeated taking into account the different fluence gradient the sample was exposed to after accounting for the energy loss at the entrance window. Since the photolyses were carried out under sub critical fluence regime, even a marginally different loss at the entrance window modified the fluence gradient quite significantly inside the cell. With all these factors taken into account, we could get a good agreement between the theoretical and experimental results obtained with both the lasers.

Table 2
Experimental conditions and results of the PCR runs[a]

Run #	Average incident energy (J)	Lens focal length (cm)	Total # of pulses	% Decomposition of 13-CF_2HCl	$^{13}V_R$ (cm^3 $pulse^{-1}$)	%13C:12C composition in the product
1	0.5	75	79200	Negligible	Nil	–
2	0.7	75	96220	6.8	0.22	40:60
3	0.7	75	86400	9.6	0.35	39:61
4	0.8	100	91700	Negligible	Nil	–
5	1.0	100	1,34,000	12.5	0.28	37:63

[a] *Note*: 50 Torr natural CF_2HCl for all the runs.

After the validation exercise in cell experiments with single pass irradiation, PCR runs were initiated using the 9 P(22) line for all the runs. Depending on the results in a particular run, photolysis conditions were altered for the subsequent run with respect to the following:

(1) Variation in the laser pulse duration:
   (a) tail-free 100 ns pulses;
   (b) 100 ns pulses with a short (~1 μs) tail or;
   (c) "normal" pulses with a 100 ns spike followed by a few μs tail;

   by changing the lasing gas mixture composition appropriately.
(2) Variation in the focal length of the focusing lens ($f = 75$ or 100 cm) and its location for launching the incident beam in the multi pass, refocusing cavity.

Table 2 summarizes the experimental conditions along with the results obtained for the PCR runs.

In run # 1, the focusing lens ($f = 75$ cm) was located inside the PCR and tail-free 100 ns pulses were used with an average incident energy of 0.5 J per pulse. Even after photolysis with 79,200 pulses, there was very little decomposition as evidenced by GC and MS analyses of the photolysed samples.

In run # 2, sample was irradiated with a higher incidence energy keeping rest of the experimental conditions the same as in run # 1. In order to achieve this with a limited pulse energy of the laser, the BaF_2 window mounted on the entrance flange of the PCR was replaced by the focusing lens. The average incident energy was 0.7 J and photolysis with 96,220 pulses gave rise to an overall decomposition in $^{13}CF_2HCl$ of 6.8% corresponding to a reaction volume, $^{13}V_R$ of 0.22 cm^3 $pulse^{-1}$ and the % ^{13}C: ^{12}C composition in the product was 40:60. The β and S values were 58 and 63, respectively.

In run # 3, sample was irradiated using 100 ns pulses with a slight tail at a marginally higher incident energy keeping rest of the experimental conditions as in run # 1. The average incident energy was 0.7 J. By photolysing with 86,400 shots, we could obtain an overall decomposition in $^{13}CF_2HCl$ of 9.6% with a reaction volume, $^{13}V_R$ of 0.35 cm^3 $pulse^{-1}$. The % ^{13}C:^{12}C composition in the product was 39:61. The corresponding values of β and S were 56 and 59, respectively.

Our previous cell experiments with a milder focusing lens ($f = 100$ cm) had yielded a relatively better $^{13}V_R$ values by

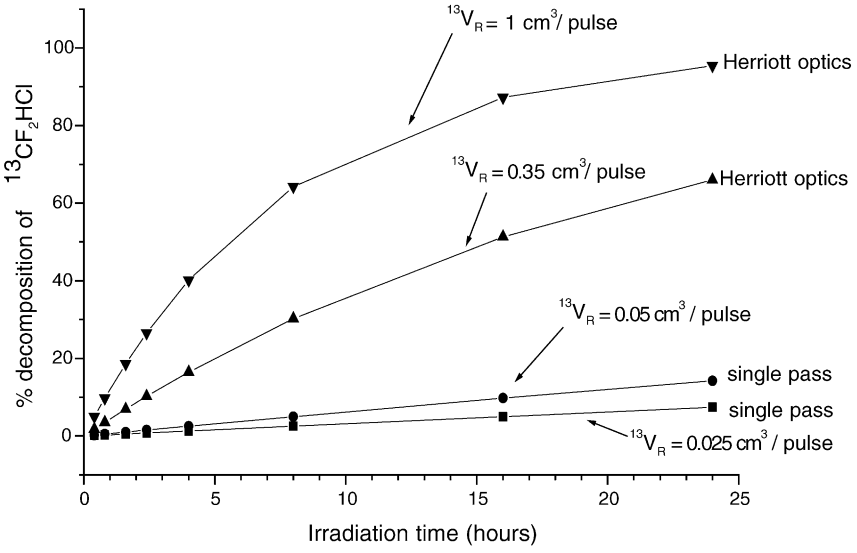

Fig. 4. Simulation of decomposition results under single and multi pass irradiation in the PCR: (■) for $^{13}V_R = 0.025$ cc $pulse^{-1}$, (●) for $^{13}V_R = 0.05$ cc $pulse^{-1}$, (▲) curve for $^{13}V_R = 0.35$ cc $pulse^{-1}$, (▼) curve for $^{13}V_R = 1.0$ cc $pulse^{-1}$.

a factor of 2–3 compared to those using $f = 75$ cm lens. This could be understood in terms of favorable "geometric factor" of the fluence gradient encountered by the sample. Therefore, with the idea of improving $^{13}V_R$ in the PCR further, run # 4 was carried out using a lens with $f = 100$ cm in place of the one with $f = 75$ cm with 100 ns pulses with a slight tail at an average incident energy 0.8 J. However, even after irradiating with 91,700 pulses, there was very little decomposition in $^{13}CF_2HCl$ as revealed by the GC and MS analyses. Apparently, increase in the irradiated volume was also accompanied with lowering of the effective fluence gradient in the multi pass cavity which would nullify any potential advantage for enhancing the overall decomposition.

In run # 5, sample was irradiated at higher incident energies achievable with the "normal" pulses, which is 100 ns spike with a few μs long tail at an average incident energy 1 J for a total number of 1,34,000 pulses. The overall decomposition in $^{13}CF_2HCl$ was found to be 12.5% and the $^{13}V_R$ was 0.28 cm^3 $pulse^{-1}$. The % ^{13}C:^{12}C composition in the product was 37:63. The product had a β value of 52 and the S value was 56.

These results successfully demonstrated that an isotopically selective decomposition is possible in a large photochemical reactor. It is quite significant considering the $^{13}V_R$ obtained (0.35 cm^3 $pulse^{-1}$) in the PCR run compared to that obtained in the cell experiments ($\sim$0.03 cm^3 $pulse^{-1}$) under single pass irradiation and similar experimental conditions. In the latter case, photolysis time would have been an order of magnitude higher to obtain the same degree of conversion, i.e., about 10% decomposition of the C-13 species in the entire PCR. This clearly demonstrates the effectiveness of the Herriott type multi pass, refocusing optics in the PCR in improving the selective decomposition quite significantly.

A simulation of the C-13 species depletion of a PCR batch as a function of the number of pulses can be evaluated using the expression (2) for both the single and multi pass cases using our experimental data and is shown in Fig. 4. It illustrates the great leverage obtained in reducing the irradiation time by deploying multi pass Herriott optics to obtain a certain degree of conversion of the C-13 species at a given selectivity. Therefore, processing of a moderate batch size of 280 l in a reasonable time can be conveniently effected by employing the multipass Herriott optics.

6. Conclusion

We have gained a lot of operational experience for successfully carrying out the LIS runs in the PCR. There is scope for further improvement in the reaction volume per pulse by judiciously adjusting the beam waist size, focal zone depth etc. for the right combination of the focusing optics and the inter mirrors' separation distance. For example, by increasing the $^{13}V_R$ further to 1 cm^3 $pulse^{-1}$ from the current value of 0.35 cm^3 $pulse^{-1}$, one can realize a 40% decomposition in the C-13 species in about 4 h irradiation time. However, even with current moderate value of $^{13}V_R = 0.35$ cm^3 $pulse^{-1}$, we would be able to induce 30% decomposition in a 8 h batch run. This would correspond to a processing of about 100 mg of carbon with a 40% C-13 content.

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