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On scaling up of carbon isotopes' enrichment by infrared laser chemistry of CF_2HCl

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Abstract

Validation studies for C-13 enrichment 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. Theoretical simulation of the reaction volume for both the cases indicated that the apparent discrepancy was due to a slight difference in cell windows' absorption for the two lasers, beam waist dimensions and the net resultant fluence gradient the sample was exposed to.

Keywords: Laser enrichment; Carbon isotopes

1. Introduction

Isotope enrichment by infrared laser chemistry has emerged as a viable method especially for the light elements during the past decade [1–5]. The expertise generated for the carbon isotopes, in particular, is adaptable to the separation of isotopes like oxygen-18 and sulphur-33 which have several important applications in medicine and biological research [6,7].

After various parametric and optimization studies on carbon-13 laser isotope separation (LIS) and some experience on the laboratory scale enrichment [8–11], we have been currently working on the macroscopic level enrichment using a large photochemical reactor (PCR) of 280 l volume and a 10 Hz pulsed CO_2 laser. The PCR consisting of a three module structure has independent gas circulation arrangement in each module and employs a Herriott type multi-pass, refocusing optics for efficient laser photon utilization [12,13].

Before carrying out the runs on a very large scale, 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 [8]. This has been shown to be a favourable system when the C-13 atom fraction in the product is limited to 50% starting from an initial natural abundance of 1.1%.

$$^{13}CF_2HCl \xrightarrow{\text{TEA } CO_2 \text{ laser}} {}^{13}CF_2 + HCl \tag{1}$$

$$2\,^{13}CF_2 \rightarrow {}^{13}C_2F_4 \tag{2}$$

Although the infrared multiple photon dissociation (IR MPD) of CF_2HCl, in principle, can give rise to higher enrichment levels in a single stage, it is possible only at the cost of product quantity. The system, however, offers a much higher throughput at moderate enrichment levels as the C-13 selective IR MPD can be performed at tens of Torr pressure level and the photon economy is excellent [14–16].

Normally a low average power (low repetition rate) laser is employed for basic parametric studies in the IR laser chemistry. In order to carry out a production run in the laser isotope separation, one has to use a higher average power (higher repetition rate) laser. These two lasers can have characteristics very different from each other. For example, aspects like difference in the temporal structure, spatial energy distribution, beam waist, spectral width etc of the two lasers can have a profound influence on the decomposition extent and isotopic

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selectivity. Moreover, in some cases, the high repetition rate lasers may deliver pulses of lower energy content and necessitate the use of tighter focusing compared to that employed in studies with lower repetition rate lasers. Such geometric factors can give rise to lower irradiation volumes and correspondingly lower throughput. Because of these reasons, it is essential to carry out validation experiments before any large scale photolysis runs are attempted. The present work describes such a study and makes use of a model to understand the difference in the results obtained for irradiation with two different lasers. Our results confirm that when a small cell experiment with a low power laser is translated for large scale photolysis with a high power laser, the scale up need not be linear with respect to the repetition rate of the high power laser for various reasons described above.

2. Experimental

Photolysis was carried out at room temperature in pyrex cells (50 and 100 cm long, volume 473 and 766 cm^3, respectively) fitted with BaF_2 windows using two independent line tunable commercial CO_2 lasers (Laser # 1, Lumonics, 0.5 W (1 J, 0.5 Hz) and (Laser # 2, Macro Optica, 10 W, 1 J, 10 Hz). The electrical discharge and optical resonators of the two laser systems were such that both the lasers delivered pulses of 80–100 ns duration without any tail. The emitted beams had a near similar divergence (~3 mrad) and longitudinal mode structure. The transverse profile consisted of a multimode structure with a near uniform intensity pattern. For a comparative study, commercial grade, natural CF_2HCl was filled at a particular pressure in a given cell, irradiated at an identical repetition rate of 0.5 Hz with both the lasers in two separate experiments using identical focused beam geometry at carefully controlled pulse energies and for the same number of laser pulses. Average energy absorption in the system was measured using two calibrated Joule meters (GenTec) with the simultaneous monitoring of pulse energies for both the reference and transmitted beams. This method minimised the measurements' error due to pulse energy fluctuation which was typically about ±5%. Absorption losses due to the cell windows for both the lasers were measured with an evacuated cell in the same way.

After photolysis, the quantity of the photoproduct, tetrafluoroethylene, (C_2F_4) and its C-13/C-12 atom fraction ratio were measured by gas chromatography (GC) (Shimadzu) and mass spectrometry (VG Elemental) respectively to obtain the specific decomposition rate of an individual isotopic species and the enrichment factor, β [8]. The latter term is defined as:

$$\beta = (^{13}C/^{12}C)\text{ ratio in the photoproduct } C_2F_4/\text{initial }(^{13}C/^{12}C)\text{ ratio} \quad (3)$$

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, β was calculated to be:

$$\beta = (2I_{83} + I_{82})98.89/(2I_{81} + I_{82})1.11 \quad (4)$$

Extent of decomposition in $^{13}CF_2HCl$ was obtained from the experimental β values along with the total product yield measured by gas chromatography.

In a typical LIS run, a laser beam propagates centrally and axially through a cylindrical cell and is focused at the cell centre while the fluence at the cell windows is kept lower than the damage threshold value for the windows which is typically about 2 J cm^{-2}. Laser induced decomposition occurs in the irradiated volume mostly near the focal zone. The dissociation extent per pulse may be expressed in terms of the cell averaged reaction volume, V_R which is defined as the product of the experimentally measured specific dissociation rate, d, for a particular isotopic species and the cell volume, V_{cell}. For example, the reaction volume for C-13 species would be $^{13}V_R = d_{13}V_{cell}$.

The term d is evaluated using the expression:

$$N_m = N_0(1 - d)^m \quad (5)$$

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

3. Results and discussion

Photolysis was done using both the lasers for various incident pulse energies and substrate pressures for the CO_2 laser lines, 9P(22) and 9P(26). The results for C-13 decomposition extent and the β values with both the systems were found to be self consistent and as per the trend reported by us in reference [8]. For example, irradiation with the 9P(22) line of either laser gave a better reaction volume per pulse ($^{13}V_R$) compared to that with the 9P(26) line. The general dependence of $^{13}V_R$ and β values on the substrate pressure, fluence and pulse duration for irradiation with a particular laser line showed a similar trend with both the lasers. 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 9P(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 (laser # 1) whereas it was about 0.05 cm^3 per pulse for excitation with the 10 W laser (laser # 2) under identical irradiation condition (Table 1). The experimental result was verified a number of times to make sure that there was no extraneous factor involved. A similar trend was observed for the 9P (26) line also.

Interestingly, for a given set of parametric conditions, the net energy absorbed in the system was found to be nearly the same with both the lasers. Therefore, this apparent anomaly

Table 1
Comparative results for irradiation with two different lasers[a]

Laser # and laser line	Average focal fluence ($\mathrm{J\,cm^{-2}}$)	$^{13}V_R$ ($\mathrm{cm^3}$ per pulse)
# 1/9P(22)	4.7	0.25
# 2/9P(22)	4.8	0.05
# 1/9P(26)	5.7	0.11
# 2/9P(26)	5.5	0.02

[a] Substrate pressure: 50 Torr; both the lasers operated at 0.5 Hz.

required an in depth analysis of the results using an appropriate model.

3.1. The model

Data analysis consists of derivation of parameters specific to the molecule from the V_R values, which in an IR MPD experiment get convoluted due to the focused laser beam geometry employed. It would ideally involve the determination of the molecular dissociation probability, q, as a function of fluence, ϕ, which is related to V_R by

$$V_R = \mathrm{d}V_{\mathrm{cell}} = \int_{\mathrm{cell}} q\,\mathrm{d}V \tag{6}$$

Many different models [17–20] have been reported in the literature for such evaluation. We have shown [20] that in single frequency IR MPD, such deconvolution can be effectively performed using two fitting parameters namely critical fluence, ϕ_c and order of the multiphoton process, n.

$$q = (\phi/\phi_c)^n \text{ for } \phi < \phi_c \tag{7}$$

$$q = 1 \quad \text{for } \phi \geq \phi_c \tag{8}$$

In this model, two important criteria such as transverse beam profile of the laser and the optical thickness of the sample need to be considered.

Since our multimode laser beam resembles a nearly uniform transverse profile, the treatment based on such beam profile has been considered. The beam envelope in the reaction cell can be expressed by

$$r^2 = r_f^2(1 + z^2/a^2) \tag{9}$$

where a is the Rayleigh range, r_f is the focal spot radius and r is the radius of the beam at a distance z from the focal point.

For an optically thin sample where the pulse energy attenuation has been insignificant, the analysis takes into account just the variation of fluence ϕ due to the focusing geometry and assumes that the pulse energy is nearly the same at any plane in the axial direction of the cell. Since the present LIS experiment involves excitation and dissociation of a minor isotopic species, (1.1% $^{13}CF_2HCl$), the sample in principle, can be treated as optically thin. However, for longer cells where there can be significant absorption due to both resonant and non-resonant isotopic species, correction needs to be applied for the attenuation of the pulse energy as the beam traverses through the cell.

As a function of the dimensionless fluence F at the beam waist, $F(\equiv\phi_0/\phi_c)$, the dimensionless reaction volume $Y(\equiv V_R/V_f)$ is given by

$$Y = F^n \int_0^{1/a} (1 + k^2)^{1-n}\,\mathrm{d}k \text{ for } F < 1 \tag{10}$$

$$Y = (F-1)^{1/2} + \frac{1}{3}(F-1)^{3/2} + F^n \int_{(F-1)^{1/2}}^{L/a} (1 + k^2)\,\mathrm{d}k \text{ for } F \geq 1 \tag{11}$$

where $V_f = 2\pi r_f^2 a$ is the focal volume, ϕ_0 is the focal fluence, L is half the cell length and $k(\equiv z/a)$ is the dimensionless axial distance.

Cell integrated reaction volume per pulse for the carbon-13 species ($^{13}V_R$) is thus computed and compared with that obtained experimentally. This exercise takes into account the incident pulse energy, beam size and its propagation under focusing inside the cell after passing through a lens. Based on the reaction probability function in a small volume element at a particular local fluence, the overall reaction volume over the entire irradiated zone is calculated. By an iterative procedure, $^{13}V_R$ is computed for an assumed critical fluence, ϕ_c and the process is repeated with different values of ϕ_c until both the theoretical and experimental values agree.

Fig. 1 gives a typical plot of the experimental results for the specific decomposition rates for both $^{13}CF_2HCl$ and $^{12}CF_2HCl$ as a function of laser pulse energy for the 9P (22) line using the 10 W laser. From the slopes of these plots, the respective multiphoton order, ^{13}n and ^{12}n were obtained. Using these data, critical fluence ($^{13}\phi_c$ and $^{12}\phi_c$) for the individual isotopic species was computed as per the procedure discussed vide supra.

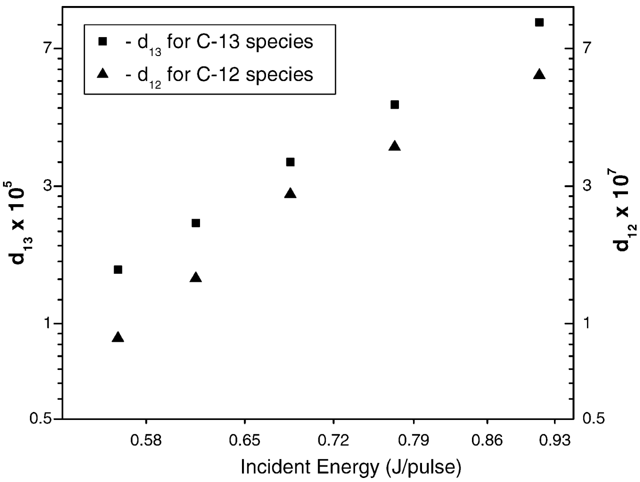

Fig. 1. Specific decomposition rates for the $^{13}CF_2HCl$ (d_{13}) and $^{12}CF_2HCl$ (d_{12}) as a function of incident pulse energy for 9P(22) line.

Table 2
Critical fluence summary for different laser lines

CO_2 laser line	^{13}n	^{12}n	$^{13}\phi_c$ (J cm^{-2})	$^{12}\phi_c$ (J cm^{-2})
9P(22)	3.5	4.0	11.5	30
9P(26)	3.5	4.0	16.0	42

Table 2 summarizes the sets of critical fluence and multiphoton order which satisfactorily explain the observed reaction conversions with both the lasers for the parametric conditions employed.

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 subcritical fluence regime, even a marginally different loss at the entrance window modifies the fluence gradient quite significantly inside the cell. With all these factors taken into account, we could observe a very good agreement between the theoretical and experimental results obtained with both the lasers.

Subsequently, we carried out macroscopic runs in the PCR using the 10 W laser and a 10% burning in the initial C-13 content was achieved after irradiating the sample for about 6 h. These runs yielded C_2F_4 photoproduct with about 40% C-13 atom fraction corresponding to a production rate of 20 mg/h. The overall $^{13}V_R$ value (about 0.3 cm^3 per pulse) confirmed the benefit of using the Herriott multi pass, refocusing optics in the PCR as compared to that obtained in the cell experiments using a single pass [13].

4. Conclusion

Our validation study showed that both the lasers gave rise to the photoproduct, C_2F_4 with about 40% carbon-13 content. However, the 10 W laser produced lesser quantity of C_2F_4 per pulse in absolute terms compared to that obtained with the 0.5 W laser. Reaction volume per pulse for the carbon-13 species ($^{13}V_R$) was computed for both the cases using the power law model for reaction probability. The theoretical values obtained were compared with the experimental values and found to agree well after taking into consideration a slight difference in the energy loss for the two lasers at the cell entrance window, beam waist dimensions and the net resultant fluence gradient available for the C-13 species in the irradiated zone.

This study shows the importance of validation exercise before any large scale operation of an enrichment scheme is attempted using a high power laser. It is imperative to confirm the results obtained with a low power laser in the cell experiments under identical conditions. Such an exercise helps in understanding of any anomalies of the results with the former system and for applying any corrective measures to be taken.

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