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Maximization of yield of C-13 isotope by multiphoton dissociation of Freon-22 using high average power TEA CO_2 laser

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Abstract. Selective multi-photon dissociation (MPD) of Freon-22 (CF_2HCl) molecules has been carried out using a TEA CO_2 laser at various CO_2 laser lines (9*P*(20)-9*P*(26)) in order to maximize the yield of C-13 isotope in the product (C_2F_4) at an enrichment factor of 100. The effects of laser pulse tail due to the presence of N_2 in the laser mixture on the enrichment factor and yield of C-13 are investigated. It is found that the addition of a small amount of N_2 is possible in the laser mixture without a significant drop in the yield at desired enrichment factor. Addition of a small amount of N_2 improves the laser efficiency considerably. At a given pulse energy, a slight change in the near field intensity distribution of a laser severely affects the selectivity of C-13 isotope. The computed far-field intensity distributions of the measured near-field intensities show marked spatial variation in the focal spots that leads to a drop in selectivity. For macroscopic production of C-13 isotope a simple and novel multi-pass cavity has been designed and tested to focus the energy repeatedly keeping the optimum fluence constant at each focal spot.

Keywords. TEA CO_2 laser; carbon-13; isotope separation.

1. Introduction

Carbon-13 is a very useful isotope in medicine and environmental studies. Modern medical science relies heavily on diagnostic procedures using C-13 labelled techniques. Diagnostic Breath Test (DBT) is one of the promising applications of the C-13 isotope.[1–3] These tests are based on the oxidation rates of special C-13 labelled preparations, which are different for healthy persons and those suffering from metabolic dysfunctions. The isotopic ratio of C-13 in the exhaled CO_2 is a measure of organic malfunction. Similarly, in environmental science, information about sources, tracks and concentrations of air pollutants is gathered by use of compounds labeled with C-13. Hence the demand for C-13 isotope is increasing day by day. Presently it is produced on the commercial scale by low temperature distillation of CO in huge liquid nitrogen-cooled columns, which takes a long time to reach the separation equilibrium and consumes a great deal of electric.[4] The growing demand for the C-13 isotope needs the development of a fast and efficient technique such as Laser Isotope Separation (LIS). The laser enrichment technique is quick because it instantly produces the enriched product. The simplicity of the enrichment set-up coupled with very high selectivity per stage makes LIS a very

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attractive technique. Freon-22 is a well-studied molecule for C-13 isotope separation[5–15] and many laboratory-scale mass-production demonstrations[16–18] have been reported. But to compete with the conventional low temperature distillation technique it is still required to maximize the yield of the desired isotope and to reduce the cost per C-13 atom separated by making the overall process more efficient.

Yield of C-13 isotope at a desired enrichment factor in the product (C_2F_4) is determined by various experimental parameters such as Freon pressure, laser fluence, pulse duration and irradiation wavelength. Freon-22 is a very nice candidate for C-13 isotope separation in a sense that it allows high-pressure irradiation, thus giving reasonable yield and better laser utilization. Basic parametric studies on Freon-22 for C-13 isotope separation using TEA CO_2 laser were carried out extensively.[5–7] In the study of Gauthier,[5] 100 Torr (~132 mbar) of Freon-22 was irradiated at various CO_2 laser lines using TEA CO_2 pulses of 80 ns (FWHM) duration. Yield of nearly 4.0% was reported at an enrichment factor of 100 using 9P(20) laser line. Higher yield of C-13 isotope using short pulses (30 mJ, 50 ns) produced by an electro-optic Q-switched CW CO_2 laser was demonstrated by Ivanenko.[8] However, higher throughput of C-13 isotope needs high pulse energy. Shorter laser pulse with higher energy (170 mJ, 40 ns) produced by employing a plasma shutter was used for C-13 isotope separation[6] but the laser efficiency was very low. The reproducibility of reliable[19] high repetition rate short pulse generation using plasma shutter may be limited.

As far as maximization of yield of C-13 isotope and the energy spent (ε) in separating a single C-13 atom are concerned, yield data and corresponding 'ε' are required to be known with respect to various CO_2 laser lines. This would help in choosing the best laser line while spending minimum photons. A good account of yield (or dissociation probability) of C-13 isotope at various lines and 'ε' is available in the work by Outhouse *et al* [7] at an enrichment factor of 100. A 10 Hz TEA CO_2 laser emitting 10 J/pulse and a pulse width of 80 ns (FWHM) was used in their work.

The objective of the present work is to increase the yield and overall efficiency of the C-13 isotope separation at an enrichment factor of 100. The two aspects that are mainly addressed are the following:

(1) At what laser line Freon-22 should be irradiated so that the yield of C-13 is maximum at enrichment factor 'β' of 100 while spending minimum photons per C-13 atom separated. (i.e. yield and enrichment efficiency is maximum).
(2) How much N_2 should be used in the laser mixture for higher laser efficiency without affecting the yield and β significantly, i.e. laser efficiency is maximum.

In the present work a high average power TEA CO_2 laser has been used which gives 130 ns (FWHM) pulses at a maximum repetition rate of 500 Hz. Since the pulse width influences the yield of C-13 isotope, it has been studied at an enrichment factor of 100 in the product (C_2F_4).

To increase the yield and efficiency of C-13 isotope using high average power TEA CO_2 laser, the yield of the isotope has been maximized with respect to laser lines, spending less photon per C-13 atom separated. To ascertain the energy efficient CO_2 laser line we have not carried out measurements similar to Gauthier,[5] rather logically inferred the most energy efficient laser line. Moreover, the economics of the process besides maximizing yield and spending less photon is also governed by the efficiency of the laser. The efficiency of the laser is greatly influenced by the concentration of N_2 in the

laser mixture. Since selective LIS requires pulses with insignificant energy in the tail, experiments have been carried out for optimum concentration of N_2 in the laser mixture so that the enrichment factor and yield are not affected significantly.

Reliable and repeatable production of an isotope, at given enrichment factor also needs a well-defined intensity distribution. A slight change in intensity distribution can totally make the process non selective. Recording the intensity distributions by a scanning pinhole and computing the far field intensity distributions using FFT (Fast Fourier Transform) qualitatively points out the sensitivity of the process to small misalignments.

Efficient production of C-13 by LIS requires efficient use of laser energy. Since a small fraction of energy is absorbed in a single enrichment step, therefore repeated use of laser energy in a pulse is required. We report here a simple and novel multi-pass imaging cavity to focus the laser beam repeatedly keeping the fluence constant at each successive spot.

2. Experimental setup

The multi-photon dissociation of CF_2HCl has been carried out using a line tunable high repetition rate UV pre-ionized TEA CO_2 laser details of which is described elsewhere.[20] The resonator consists of a concave ZnSe output coupler (reflectivity = 85%) of 5 m radius of curvature (ROC) and a grating having 150 lines per mm. Various lines in the 9·6 μm and 10·6 μm bands can be tuned by changing the angle of the grating. The laser emit pulses with an initial spike of about 130 ns (FWHM) duration followed by a long tail whose duration is mainly governed by the amount of N_2 in the laser mixture.

Generally, for the selective multi-photon dissociation, it is preferred to have tail-free pulses, which is produced by using N_2 free laser mixtures. But it drastically reduces the efficiency of the laser. The shape of the pulses, without and with nitrogen, is shown in a later section. To improve the stability of discharge and pulse energy, a small amount of H_2 is also added to the laser mixture. Most of the experiments were carried out with laser

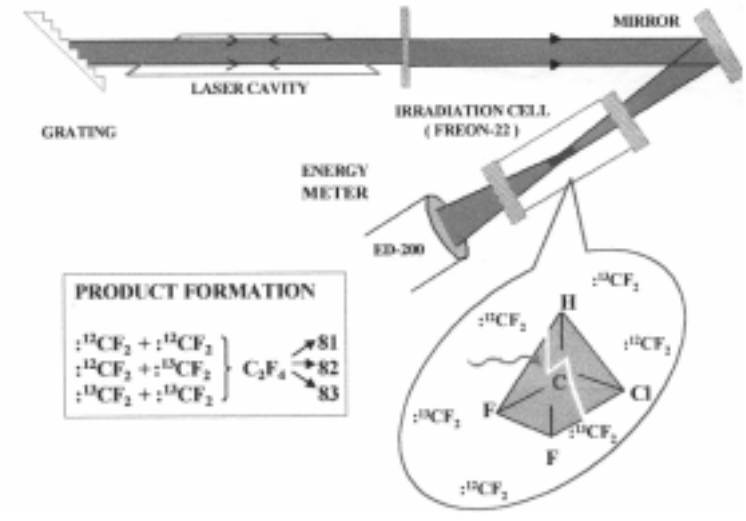


Figure 1. Schematic drawing of C-13 isotope separation process.

mixture CO_2:N_2:He:H_2::140:10:630:15 mbar. The pulse-to-pulse energy stability is ± 1·4%.

Since the unfocussed laser beam fluence is much smaller than that required for carrying out multi-photon decomposition, the beam is focussed with a mirror of 50 cm ROC kept at an angle of 10·5°. Interaction takes place near the focal zone in a small irradiation cell of volume 88 ml. The schematic arrangement of the laser and irradiation cell is shown in figure 1. After irradiation, a Quadrapole Mass Analyzer (QMA) used to measure the enrichment factor in the product (C_2F_4) and a Gas Chromatograph (GC) with Porapak-Q column is used to measure the amount of the product formed. It must be noted that yield plotted in all the graphs refers to the *overall yield* of the product (C_2F_4) formed after irradiation with a certain number of pulses.

3. Infrared multi-photon dissociation of Freon-22

The natural abundance (α) of C-13 is only 1·11%. When photons of appropriate wavelength and fluence interact with the CF_2HCl molecule the ν_3 vibrational mode corresponding to C–F stretch[21] absorb several photons resulting in its dissociation. The isotopic shift between $^{12}CF_2HCl$ and $^{13}CF_2HCl$ molecules is 24 cm^{-1}. The C-13 bearing $^{13}CF_2HCl$ molecules can be selectively dissociated by an appropriate choice of laser line in the 9*P* band of a CO_2 laser. The dissociation process and product formation take place as the following:

$$CHClF_2 \xrightarrow{nh\nu=56\,\text{kcal/mole}} :CF_2 + HCl, \quad :CF_2 + :CF_2 \rightarrow C_2F_4.$$

Depending upon the ratio of C-13 and C-12 bearing molecules in the product (C_2F_4) and in the reactant (CF_2HCl) the enrichment factor[6] β is defined as:

$$\beta = (^{13}C/^{12}C)\ \text{product}/(^{13}C/^{12}C)\ \text{reactant}.$$

Since we have used QMA to detect the product at mass numbers 81, 82 and 83 corresponding to ^{12}C–^{12}C, ^{12}C–^{13}C and ^{13}C–^{13}C atom combinations respectively, the formula for enrichment factor[9,10] becomes:

$$\beta = \{(1-\alpha)/\alpha\}\ \{[2P_{83} + P_{82}]/[2P_{81} + P_{82}]\},$$

where, P_{81}, P_{82} and P_{83} are partial pressures corresponding to mass numbers 81, 82 and 83 respectively as detected by QMA.

We define here a term *overall yield* denoted by symbol *X*. This quantity gives total amount of C_2F_4 produced after *m* number of pulses. The QMA can also be used to measure the overall yield of the C_2F_4 by adding the partial pressures corresponding to mass numbers 81, 82 and 83. In all our experiments we have measured the overall yield of the product using this method. The overall yield obtained by QMA by this method is found to be proportional to that obtained by using GC. A typical comparison of overall yield obtained by GC and QMA is presented in the appendix. For relative comparison overall yield is a good parameter but to know yield or yield per pulse *Y* (i.e. ratio of number of C-13 molecules dissociated to the number of C-13 molecules irradiated per pulse) a sample calculation is also presented in the appendix using GC data.

4. Results and discussions

We present here the experimental results of our study on the effect of various parameters such as Freon pressure, laser fluence, laser pulse shape and irradiation wavelength on the enrichment factor and yield of C-13 isotope. Since the TEA laser emits multimode beam with a pulse width of 130 ns, it is required to find out the optimum Freon pressure for our case as the optimum pressure depends on the pulse width.[22] Freon-22 samples at different pressures were irradiated by the conventional 9*P*(22) line at fixed fluence of 5·35 J/cm^2. The optimum pressure in our case is 100 mbar, which gives high β as well as high yield. A further increase in pressure reduces β drastically. This is due to the collisional transfer of energy from resonant isotope (C-13) to non-resonant isotope (C-12) during the laser pulse resulting in dissociation of undesired C-12 isotope thus reducing β in the product. For all the optimization experiments we have therefore kept the Freon pressure at 100 mbar.

4.1 *Maximization of yield*

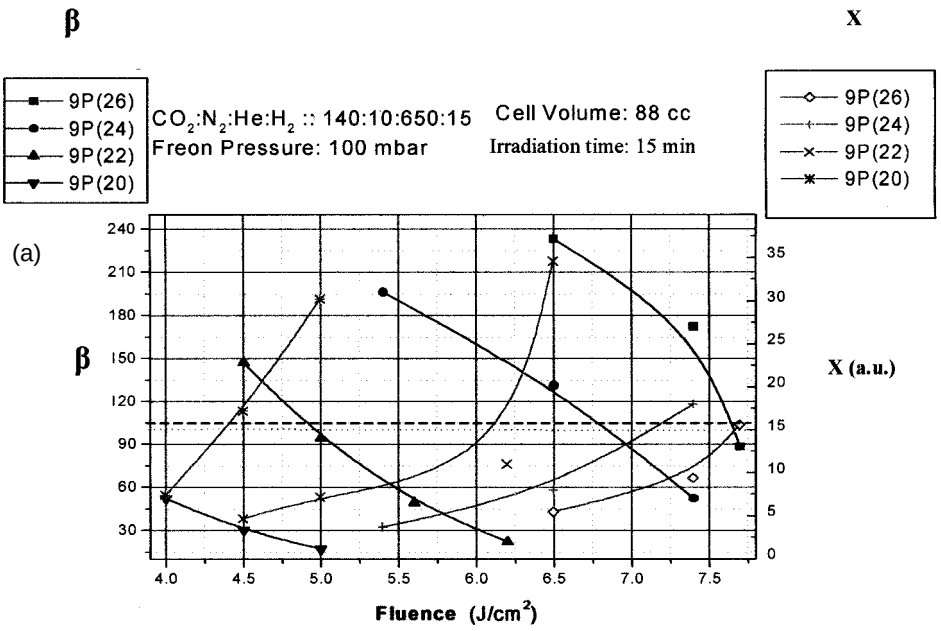
We wanted to find out for which laser line the yield is maximum for an enrichment factor (β) of 100. Freon gas samples were therefore irradiated at various lines from 9*P*(20) to 9*P*(26). X and β were measured using QMA and plotted as a function of fluence for various laser lines. The results are presented in figures 2a and b.

It has been observed that for a given laser line, β is high at low fluence and it drops down as fluence increases. This is because of power broadening, which at low fluence brings C-13 bearing CF_2HCl vibrational levels preferentially in resonance with the virtual levels. The virtual levels are the non-stationary states of a molecule, which are created at high intensity leading to absorption of many photons. The virtual levels basically provide a short-lived pathway for dissociation of molecules via multi-photon absorption. This causes higher yield of C-13 molecules compared to the yield of C-12 bearing molecules in the product (C_2F_4). As the fluence increases the near resonance condition is also satisfied for vibrational levels of C-12 molecules whose concentration is nearly 100 times more, thus its dissociation increases substantially leading to drop in β. From figure 2a we can extract overall yield of C_2F_4 having 50% C-13 atoms (β = 100) at various laser lines. The results are summarized in figure 2b. The fluence required to obtain a β of 100 at each line is also mentioned in the same plot.

Using the data from figure 2b the yield Y can be calculated (see appendix) for all the laser lines. We can see that as we shift from 9*P*(20) to 9*P*(26) the yield of C-13 increases and so also the operating fluence. The yield of C-13 at 9*P*(26) line is more than double than that at 9*P*(22) line. However, energy requirement at 9*P*(26) is just 1·5 times more than at 9*P*(22). This logically implies that enrichment efficiency has increased as we move towards the red edge of the C-13 absorption band. Towards red edge of the absorption spectrum of C-13 isotope relatively higher fluence is required to bring the vibrational levels in near resonance with the virtual levels. Once near resonance condition is achieved the reaction probability increases nonlinearly with the fluence.[11,23] At the same time towards the red edge of the C-13 absorption curve, the absorption of C-12 is relatively weak and even at higher fluence it does not contribute much allowing higher yield of C-13 isotope at desired β. In conclusion, higher operating fluence towards the red edge leads to better enrichment efficiency. Outhouse *et al* [7] also reported a similar trend. This suggested to us that lines further towards red of C-13 absorption curve (such as

9*P*(30) or 9*P*(32)) should be used. We could not try these lines because the fluence required to have β of 100 could not be achieved under our experimental conditions.

Another advantage of using lines towards red edge is related to linear absorption coefficient. The linear absorption coefficient[12] of 9*P*(26) line in CF_2HCl is almost half of that at 9*P*(22) line. This gives another benefit when the energy in a laser pulse has to be used repeatedly for multi-photon dissociation. This will be further discussed in §4.4.



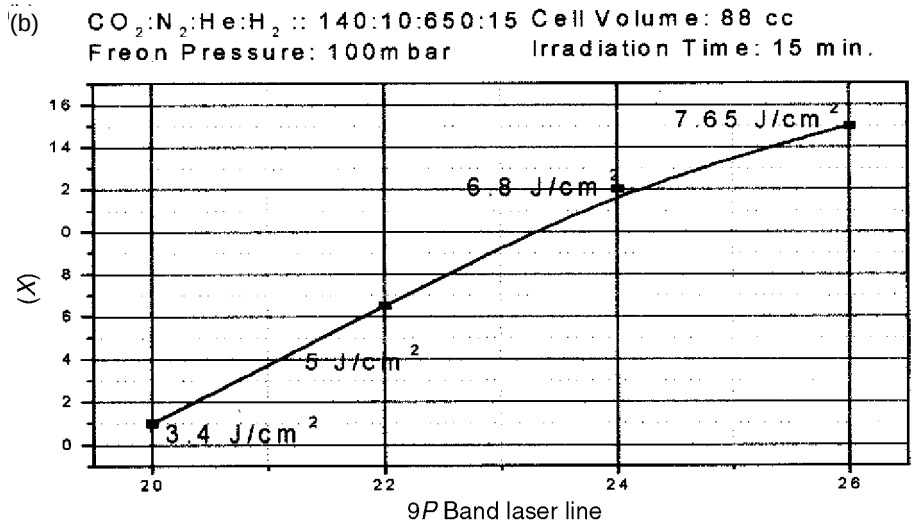


Figure 2. (**a**) Variation of β and X for various laser lines with respect to laser fluence. (**b**) Overall yield of C_2F_4 at β of 100 for various laser lines.

4.2 *Maximization of laser efficiency*

CO_2 laser efficiency is greatly affected by the presence of N_2 in the laser mixture. Normally the pulse emitted by TEA CO_2 laser has an initial narrow spike followed by a long tail mainly because of the slow pumping of the upper laser level of CO_2 molecule by N_2. The energy residing in the tail is deleterious for the selective multi-photon dissociation. However, we have observed that up to a certain concentration of N_2 in the laser mixture the energy in the tail is not significant and the enrichment factor and yield of C-13 at a given fluence is not affected much. But if N_2 concentration is further increased the enrichment factor drops down drastically.

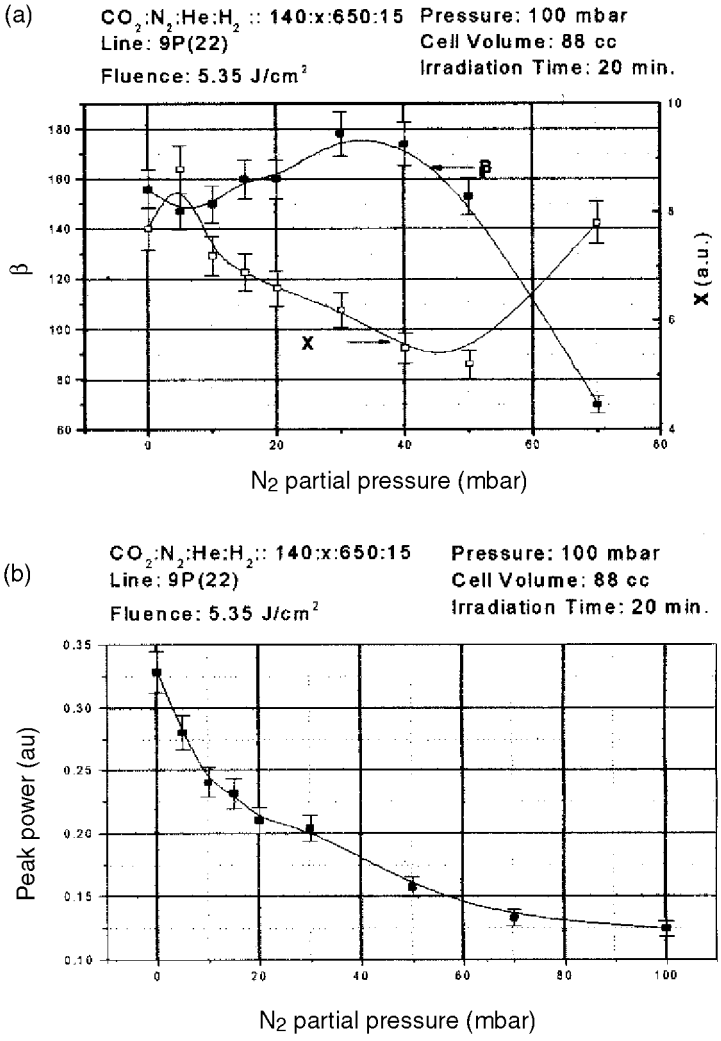


Figure 3. (**a**) Variation of β and X for different partial pressures of nitrogen in the laser mixture at constant fluence. (**b**) Laser peak power for different partial pressures of nitrogen in the laser mixture at constant fluence.

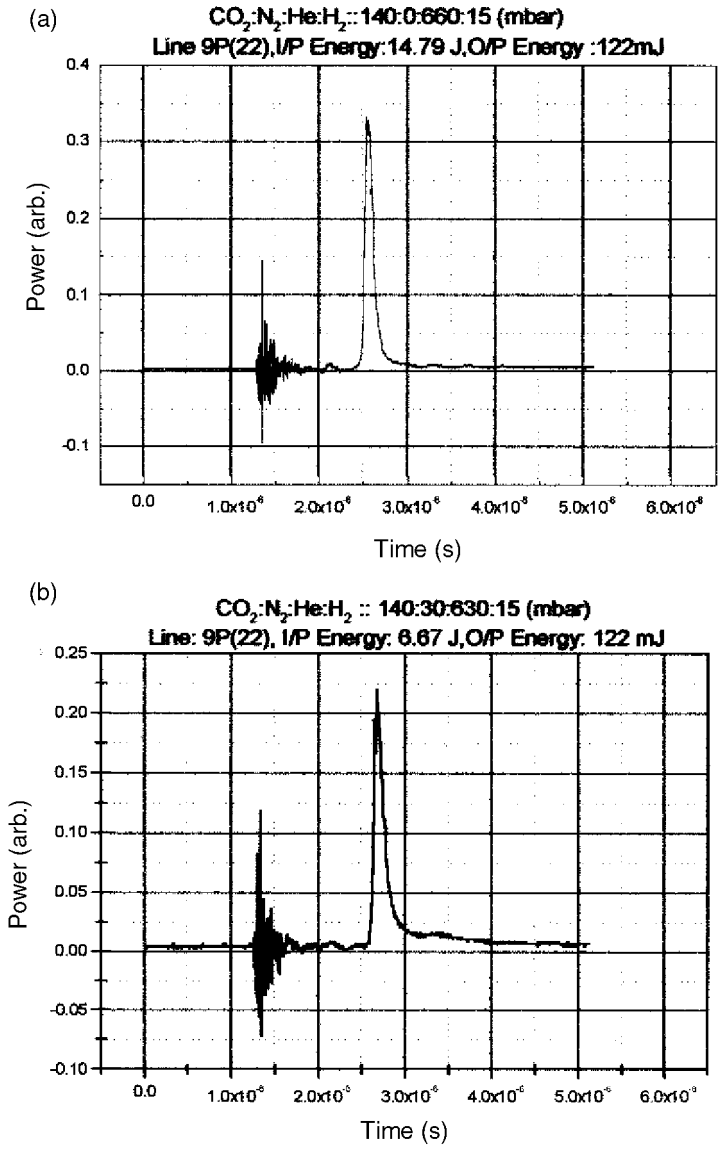


Figure 4. Laser pulse shapes for 0 (**a**) and 30·0 mbar (**b**) of nitrogen in the laser mixture.

We have irradiated 100 mbar of Freon sample at 9*P*(22) line and at constant fluence for varying concentration of N_2 in the laser mixture. The results are presented in figure 3a. The laser pulse shapes for different concentration of N_2 in the laser mixture and at constant fluence have been presented in figure 4.

It can be seen that with increase in N_2 partial pressure the β, first increases and then drops drastically when N_2 pressure is increased beyond 30 mbar. This observation is not in line with the assumption that with increase in N_2, β drops down. In order to resolve

this we have recorded the laser pulse shape at a constant fluence for different concentration of N_2 in the laser mixture. At a constant laser pulse energy, the peak power of the initial spike decreases gradually with increase in N_2 and the energy in the tail portion goes on increasing keeping total area under the curve the same. The peak power versus N_2 concentration is also shown in figure 3b. The reason for initial increase in β and drop in X can be explained by the fact that with increase in N_2 the peak intensity reduces and energy going in the tail portion is not effective to enhance the yield of collisionally excited C-12 molecule to cross the dissociation barrier. We can see that in this case the initial spike only decides the yield, as the tail energy is not contributing to dissociation of either of the isotope. However when N_2 concentration is more, the energy residing in the tail is sufficient to pump the collisionally excited C-12 molecules to cross the dissociation barrier thus increasing its yield and a sudden drop in β. This increases overall yield of the product but β is low.

Under a typical set of experimental conditions, β of around 160 is maintained till 30 mbar of nitrogen is added to the laser mixture. However the overall yield drops only by about 10% when 30 mbar of nitrogen is used compared to its value when no nitrogen is used in the laser mixture. It can be concluded that about 30 mbar of N_2 can be safely added to the laser mixture (CO_2:N_2:He:H_2::140:x:630:15 mbar, x = N_2 partial pressure) without a significant change in the β and X. The increase in efficiency of the laser when 30 mbar of N_2 is added is more than 120% compared to that when no nitrogen is used in the laser mixture. Higher efficiency of the laser reduces the cost of photons and hence makes the overall process more economical. The optimum laser gas mixture which can be used for selective MPD is CO_2:N_2:He:H_2::140:30:630:15 mbar.

4.3 *Effect of intensity distribution*

During C-13 enrichment experiments it was observed that at a given fluence (calculated by dividing the laser energy by measured spot size on the paper), and keeping other parameters same, selective MPD of Freon-22 sometimes becomes non-selective. The view graphs of Quadrapole Mass Analyzer under same set of experimental conditions are shown at the bottom of figure 5. The β in one case is 150, which drastically drops down to 20 under the same set of experimental conditions. This suggested us that there is some other parameter besides those, which were considered, which affects the enrichment factor. Critical observation revealed that the intensity distribution in both cases were slightly different. The burn patterns obtained on the thermal paper at different locations away from the output coupler are also shown at the top of the figure 5.

To qualitatively explain the difference, the near-field beam intensity distributions were measured using a scanning pinhole and a pyroelectric detector. The measured near-field intensity distributions in two cases are presented in the same figure. Computed far-field distributions using the FFT technique show marked difference in spatial distributions at the focal spots. We can see that in the case where the intensity distribution is slightly asymmetric the effective focal spot diameter is smaller, thus increasing the effective fluence, which reduces the selectivity and hence β. This reduction in focal spot diameter could not be resolved by measuring the burnt hole in the paper kept at the focal point. This change in intensity distribution might be due to slight misalignment of the resonator optics. Thus, besides other parameters intensity distribution should also be considered as an important parameter that might influence the selectivity and yield of desired isotope.

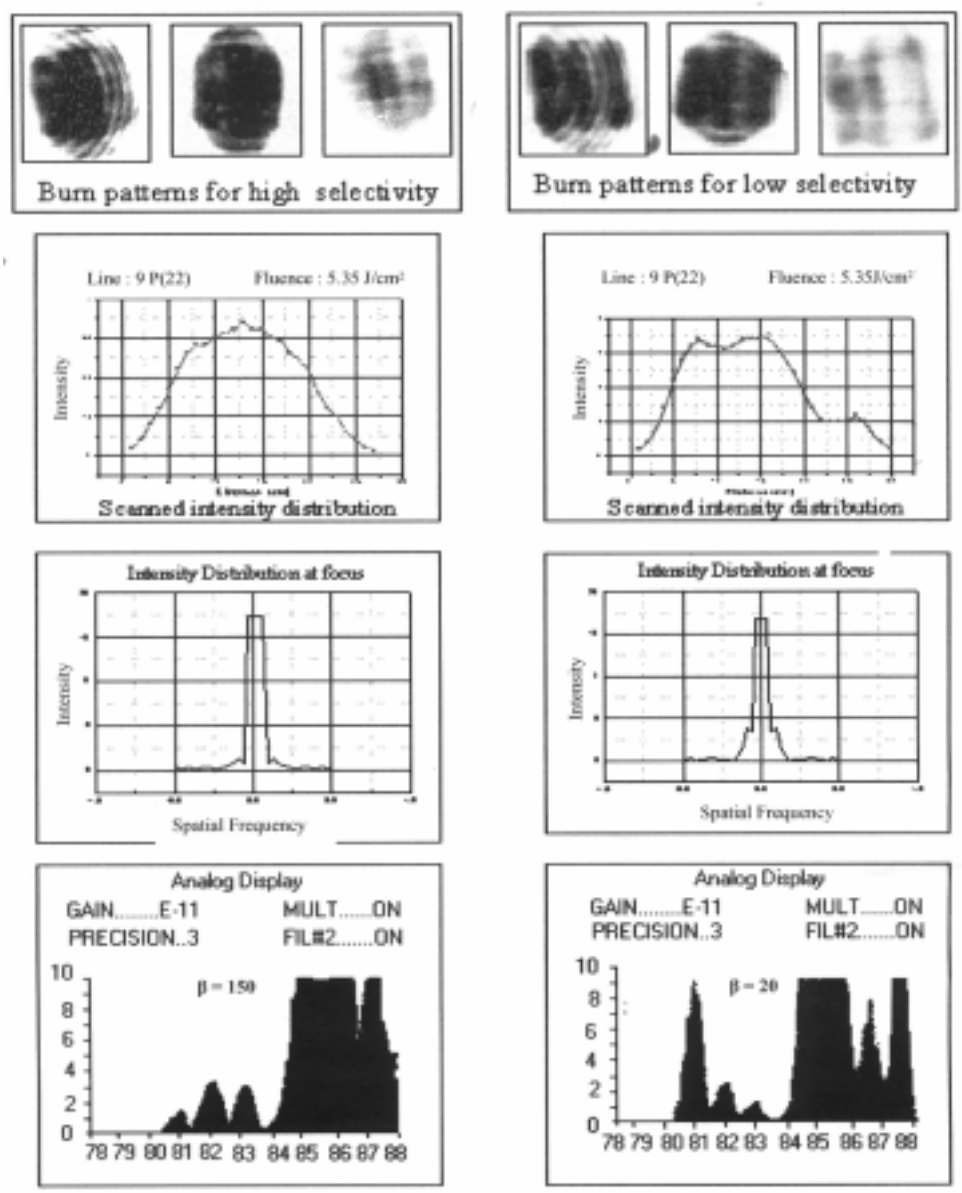


Figure 5. Beam intensity pattern and its effect on β at constant fluence.

4.4 *Multi-pass cavity design*

In a single pass irradiation set up as shown in figure 1, a small fraction of total energy in the pulse is utilized because of the low absorption cross-section of 9*P* band lines in CF_2HCl. Out of the total energy absorbed in single pass a small fraction of energy goes for MPD of Freon around the focal zone, while the rest is absorbed by the medium via linear absorption or transmitted.

Efficient utilization of laser pulse energy requires repeated focusing of laser beam till a major part of energy is absorbed in the medium. We have designed a multi-pass cavity having a number of mirrors, which focuses the beam such that:
(a) The energy lost via linear absorption is minimal. This energy does not contribute to MPD.
(b) At each successive focal zone the focal spot size reduces by a specified amount so that the optimum fluence can be kept constant.

The mirror arrangement and the beam path, using a He–Ne laser beam is shown in figure 6. In order to satisfy first condition we have used mirrors of small ROC (10 cm) so that the beam after focussing by a mirror quickly regains its size without losing much energy by linear absorption. In §4.1 we have shown that the use of lines towards the red edge increases the enrichment efficiency. At the same time the low linear absorption cross-section of these lines in Freon reduces the energy lost away from the focal zone via linear absorption. This is particularly advantageous in a multi-pass set-up because most of the time beam spans a linear absorption region.

The second condition of optimum fluence at the focal spot is very important in a sense that the yield of the desired isotope is a strong function of fluence. A drop in the fluence below optimum value may enhance the selectivity but will reduce the yield. We are aiming here at high yields of C-13 isotope at an enrichment factor of 100, which requires an optimum fluence as shown in figure 3b. After each stage some amount of energy is lost by absorption in the medium (linear + multi-photon absorption) and absorption at each mirror. It is, therefore, desired to reduce the spot size so that the fluence can be kept close to optimum value at each successive stage. This has been achieved by a very simple and novel technique. The basic principle is, when the object is at a distance equal to 2*f* (where *f* is the focal length of the mirror), then its inverted image of equal size is also formed at 2*f*. However, when the object is moved away from 2*f* then inverted image

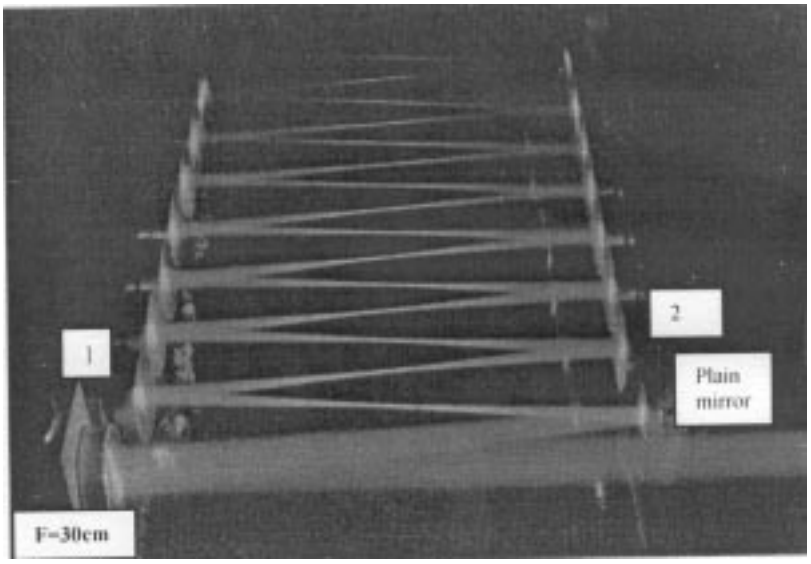


Figure 6. Simulated He–Ne laser beam path in the multi-pass cavity.

smaller in size is formed between f and $2f$. This simple principle is used to design the multi-pass cavity with gradually reducing spot size. The distance by which the object is displaced beyond $2f$ governs the reduction in spot size. Hence, depending upon the total loss of energy per stage (medium absorption + mirror absorption), the object can be displaced beyond $2f$ by a known amount so that the desired spot size can be produced and fluence can be maintained constant at each focal point.

As shown in figure 6 the unfocussed beam from the laser is first incident on a mirror of 30 cm focal length. This mirror along with a plane mirror focuses the beam in front of the 10 cm ROC mirror. This focal spot serves as an object for mirror labeled '1' which forms the image in front of mirror labeled '2'. If the first object is at a distance more than $2f$ then the image formed is smaller than its object and is between f and $2f$. The image formed by mirror '1' acts as virtual object (at a distance more than $2f$) for mirror '2', which again reduces the spot size. This process of reduction in spot size continues and the condition for reduction in spot size is automatically satisfied. We have checked the reduction in spot size using pulsed CO_2 laser beam and it matches very well with the theoretically calculated spot sizes.

The multi-pass cavity is the heart of the irradiation cell that has gas flow arrangement to facilitate high repetition rate irradiation of Freon-22 for gram quantity yields of C-13 isotope. Other details of irradiation cell and gram production of C-13 isotope will be presented in a forthcoming publication.

5. Conclusion

The efficiency of laser isotope separation of C-13 can be improved by improving enrichment efficiency. This is achieved by irradiating the Freon gas towards the red edge of the absorption curve of the C-13 isotope. This allows high fluence irradiation of Freon gas at a given enrichment factor. Higher operating fluence gives higher enrichment efficiency because of nonlinear dependence of yield on fluence. The efficiency of laser is improved by adding 30 mbar of N_2 to the laser mixture (CO_2:N_2:He:H_2::140:30:630:15 mbar) without significant effect on the enrichment factor and the yield of C-13 isotope. Addition of N_2 increases the laser efficiency, thus making the overall process economical. It has been also observed that, besides other parameters, the intensity distribution of a multimode TEA CO_2 laser beam is a very important parameter. At a given energy a slight change in intensity distribution can make the MPD process totally non-selective. Efficient macroscopic production of C-13 by LIS technique requires efficient use of energy in a laser pulse. A multi-pass cavity has been designed to efficiently utilize the energy and to keep the fluence near the optimum value at each focal spot.

Acknowledgements

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Appendix A

Overall yield data

We have carried out MPD of Freon at 9*P*(22) line and the overall yield has been measured with the help of GC as well as QMA. The yield of C_2F_4 is plotted below as a function of fluence for both cases. The overall yields obtained from GC and QMA show the same behaviour except for a constant factor (figure A1).

It must be noted that QMA basically detects $C_2F_3^+$ ions corresponding to mass numbers 81, 82 and 83. The overall yield obtained by QMA is the sum of the partial pressures at these mass numbers.

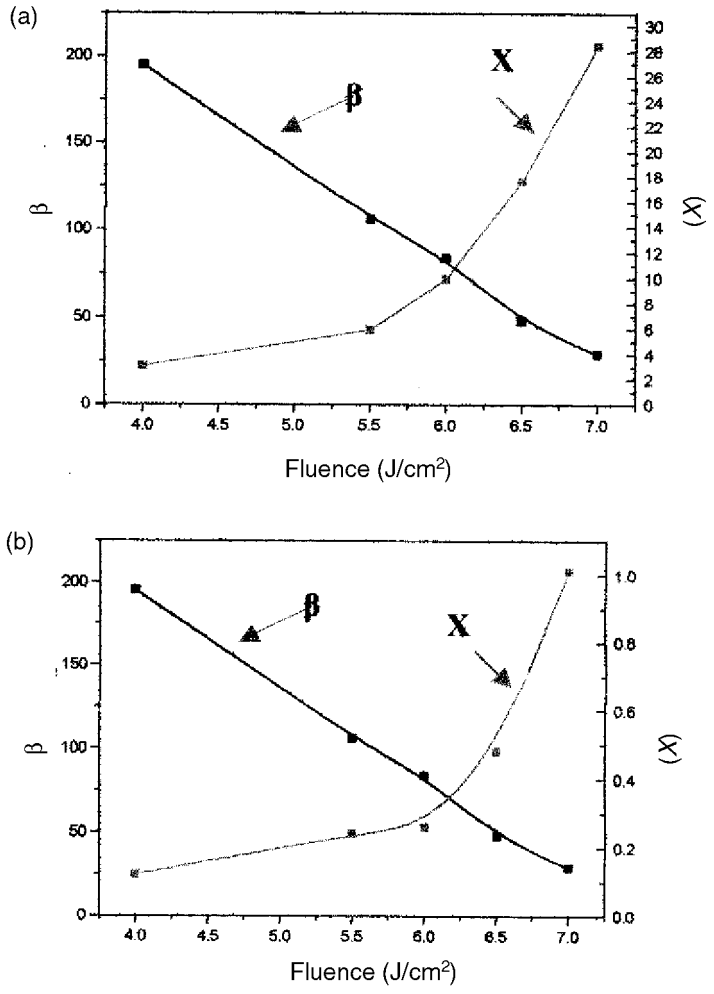

Figure A1. Comparison of overall yield obtained by QMA (**a**) and GC (**b**).

Calculation of yield

The yield or yield per pulse of C-13 isotope can be expressed as[9]:

$$Y^{13} = [1-(N_m/N_0)^{1/m}][V_{cell}/V_{int}],$$

where, N_0 is the number of C-13 molecules in the reactant (CF_2HCl) before irradiation, N_m is the number of C-13 molecules left in the reactant (CF_2HCl) after irradiation by m number of pulses, V_{cell} is the irradiation cell volume and V_{int} is the interaction volume.

N_0 = 0·0111 N, (N = total number of freon molecules per ml); N_m = 0·0111 N (1-fraction of C-13 bearing freon molecules dissociated); V_{cell} = 100 ml (including the connecting tubes and optics); V_{int} = 0·056 ml (= 0·0227 $cm^2 \times 2{\cdot}5$ cm); m = 5400; β = 100.

The yield calculated using (A1) and other relevant parameters are summarized in table A1.

Typical GC data

Typical GC data are shown in figure A2.

The first narrow peak corresponds to C_2F_4 (product) and the broad peak indicates CF_2HCl (reactant). The two components arrive at a time difference of nearly 2·55 min in a Porapak-Q column (column temperature = 80°C, carrier gas = helium, detector = TCD).

Table A1. Calculated value of yield for 9*P*(22) and 9*P*(26) laser lines at β of 100.

Laser line	X (QMA)	X (GC)	% Dissociation	Y^{13} (%)	β	Fluence (J/cm^2)
9*P*(22)	6·5	0·20	9·90	3·4	100	5·00
9*P*(26)	15·0	0·43	19·36	7·1	100	7·65

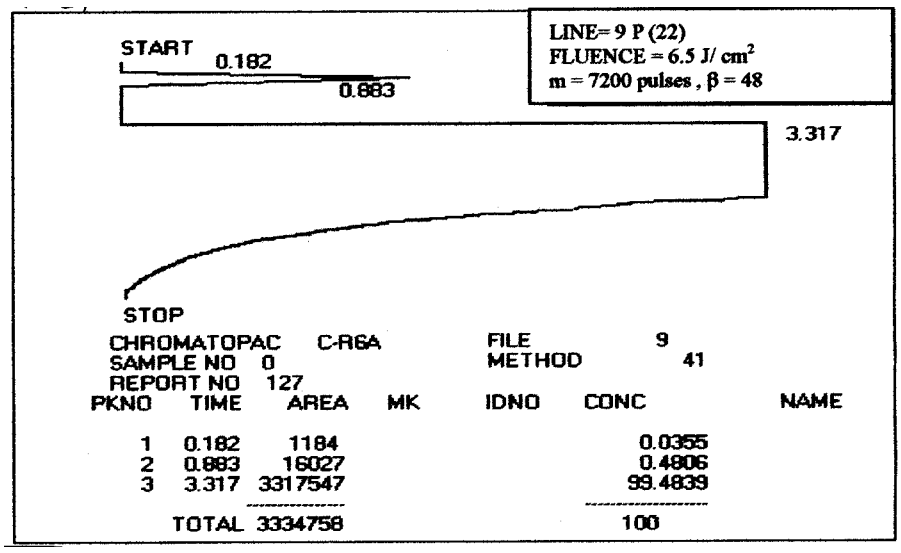

Figure A2. Typical gas chromatograph for irradiated freon-22 sample.

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