

Control strategies for laser separation of carbon isotopes

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Abstract. Laser isotope separation (LIS) by infrared laser chemistry of polyatomic molecules has come a long way since its discovery. The last decade has seen considerable efforts in scaling up of the process for light elements like carbon, oxygen and silicon. These efforts aim at ways to improve both the enrichment factor and the throughput. The achievement is quite significant especially for carbon isotope separation wherein macroscopic operating scales have been realized. We report our studies on the IR laser chemistry of two promising systems, viz. neat CF_2HCl and $\text{CF}_3\text{Br/Cl}_2$. We have investigated conditions for optimizing the dissociation yield and selectivity using natural samples containing 1.1% C-13. We also highlight our current efforts for scaling up the process. These include the design aspects of a photochemical reactor with multipass refocusing Herriott optics for efficient photon utilization, 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.

Keywords. Carbon isotopes; IR MPD; laser enrichment.

1. Introduction

The element carbon has eight isotopes ranging from C-9 to C-16. Among these, we are concerned with the separation of only those which have stable nuclei, viz. C-12 and C-13. The minor isotope C-13 with a natural abundance of 1.1% has many important applications. It is a valuable tracer in chemical, biological and environmental science.^{1–3} A number of C-13 labelled 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, early detection of *Helicobacter pylori* is possible.⁴ This organism is responsible for stomach ulcers which when undetected can lead to stomach cancer. By using $^{13}\text{CO}_2$, $^{13}\text{CH}_3\text{OH}$ and $^{13}\text{CF}_3\text{Br}$ as working media, we can have isotopically labelled gas lasers extending the tunable range in the near- and far-IR regions.

When 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

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natural diamond containing 1.1% of C-13.⁵ Such material has potential use as a 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 hundreds of kilograms per year.⁶ The current world production of C-13 at 99% concentration is only a few tens of kilograms 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 significantly capital intensive.

2. Laser isotope separation schemes

In the late seventies, several groups all over the world investigated the IR laser chemistry of trifluorohalomethanes⁸⁻¹² 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 for the carbon isotopes which can be readily excited by a pulsed CO₂ laser. The C-13 selective infra-red, multiple photon dissociation (IR MPD) of these simple molecules is as follows:



C-13 enrichment in the product, C₂F₆, was successfully demonstrated at very low pressures and low temperature. There are, however, some major disadvantages with this system. Since the rate of formation of the product in step (2) nearly equals the rate of recombination of the dissociated fragments in step (3), the overall dissociation yield is very low. Operation at higher energy density (fluence) to increase the yield severely degrades the enrichment factor. Also, the product throughput is quite small as the substrate pressure is less than 1 Torr.

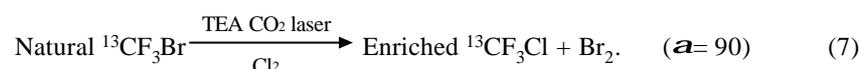
Subsequently, two viable schemes were developed. The first one developed at the National Research Council, Canada,¹³⁻¹⁵ is good for getting 50% enrichment at macroscopic levels. In this, ¹³CF₂HCl at its natural concentration in chlorodifluoromethane, undergoes IR MPD giving rise to difluorocarbene, CF₂ and hydrogen chloride, HCl. The ultimate end product is tetrafluoroethylene, C₂F₄ with a C-13 atom fraction of 50%.



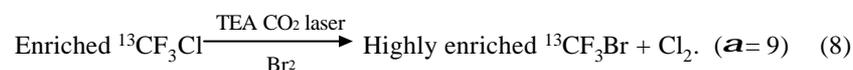
Although this system is capable of giving higher enrichment levels in a single stage, it is at the cost of product quantity.

The second one, known as Lausanne-Zurich (L-Z) cyclic scheme^{16,17}, makes use of a two-stage, closed chemical cycle and is very useful for getting high enrichment level. If we need a product with better than 90% C-13 enrichment in a single stage from the initial 1.1% level, we would require a dissociation selectivity, α better than 800. Such conditions exist only at very low pressures giving rise to very low throughput. In the L-Z scheme, the problem is split into two parts. Stage 1 aims at a large throughput limiting the enrichment to about 50%. The product from stage 1 is recovered and employed in stage 2 leading to higher enrichment. Following is the IR laser chemistry of L-Z scheme:

Stage 1:



Stage 2:



The L-Z scheme, by employing an appropriate halogen scavenger in the first stage, overcomes the recombination problem encountered in the neat CF_3X MPD (*vide infra*, step (3)) resulting in better dissociation yield. It also helps in closing the chemical cycle to obtain a product which will be a useful starting material in the second stage for further enrichment.

3. Optimization studies

We made a comparative study of both the systems.¹⁸ Our results showed that both the systems consume a similar amount of energy to get a product with about 65% C-13 content. The CF_2HCl system, however, has better photon utilisation compared to the halogen scavenged system when the enrichment is limited to 50% level. An important finding of our energy absorption studies was that the energy consumption for separating a C-13 atom (about 1.5 KeV) by the laser chemistry is nearly similar to that by the cryo distillation method.

Following are the experimental details of the laboratory scale preparation of the C-13 enriched materials at BARC^{18,19} under optimized conditions:

(a) C-13 Enrichment: 50% (neat CF_2HCl MPD)

Substrate pressure: 100 Torr
Irradiation frequency: 1047 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
Product isolated: C_2F_4 (C-13 content = 50%)

Analysis: Gas chromatography (GC) and mass spectrometry
Product separation: By GC (batch process).

(b) *C-13 Enrichment*: >95% (two-stage process)

Stage 1: Natural $\text{CF}_3\text{Br}/\text{Cl}_2$ 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
Product isolated: CF_3Cl (C-13 content = 50%).

Stage 2: Enriched $\text{CF}_3\text{Cl}/\text{Br}_2$ 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
Product isolated: CF_3Br (C-13 content > 95%).

Common to both stages:

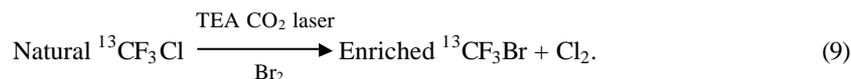
Analysis: Gas chromatography (GC) and mass spectrometry

Product separation: By cryogenic distillation followed by GC (batch process).

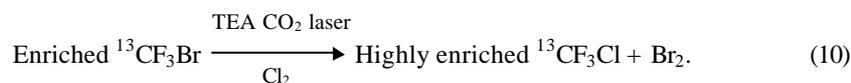
Using the above conditions, laboratory scale quantities of different enriched materials have been obtained.

In an interesting example of laser induced chemical synthesis²⁰ using the two stage, closed chemical cycle approach, we could successfully prepare, highly enriched CF_3Cl with a C-13 content of better than 97%. For achieving this, the following strategy was adapted. In principle, we could have reversed the sequence of the reactions (7) and (8).

Stage 1:

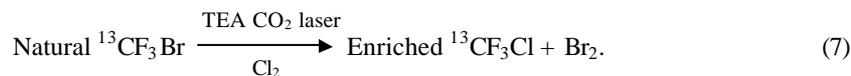


Stage 2:



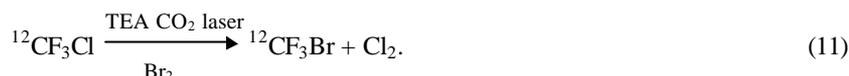
The inherent disadvantage of such a scheme is that one has to handle a large quantity of the highly corrosive bromine in step (9) which is not desirable. As an alternative, we stuck to reaction (7) and obtained 50% enriched CF_3Cl as earlier:

Stage 1:



After isolating the enriched CF_3Cl , $^{12}\text{CF}_3\text{Cl}$ present to the extent of 50% was selectively targeted and 'burnt' in stage 2 by selectively tuning the laser frequency to its absorption in the presence of a small quantity of bromine.

Stage 2:



When bulk of the $^{12}\text{CF}_3\text{Cl}$ was converted into $^{12}\text{CF}_3\text{Br}$, the residual starting material in stage 2 became highly enriched in $^{13}\text{CF}_3\text{Cl}$ with its C-13 content as high as 97% and could be readily isolated.²⁰ This example shows the flexibility of the laser induced synthesis in preparing highly enriched materials.

Subsequently we focused our attention to aspects other than the laser chemistry which would enhance the overall throughput of an enriched product. These include MPD studies in waveguide reactors,²¹ use of short duration pulses for excitation²² etc.

We used both pyrex and gold coated copper waveguides as photolysis cells in which the CF_2HCl MPD was investigated. With a careful propagation of the beam in the waveguide, one can repeatedly obtain a multiple refocusing of the laser beam compared to a single focusing in the normal cylindrical cell. The key results were that it was possible to carry out isotopically selective dissociation in these waveguides and there was a small but significant increase in the decomposition yield compared to that in the normal cell.

Normally the C-13 enrichment is obtained with the CF_2HCl system at pressures lower than 100 Torr using the tail-free, CO_2 laser pulses which have a duration of 100 ns at full width at half maximum (FWHM). Above this pressure limit, severe selectivity loss takes place due to energy transfer in collision processes between the C-13 and C-12 bearing molecules scrambling the excitation selectivity. Either by operating at lower substrate pressure or shortening the pulse duration, one can minimize the number of such collisions during excitation. Since higher substrate pressure gives rise to larger throughput, it would be better to employ short duration pulses. For example, using pulses of about 40 ns duration, we have shown²² that it is possible to maintain the same enrichment level for photolysis at 250 Torr as compared to that at 100 Torr pressure. Such short pulses have been conveniently generated by us using the laser induced dielectric breakdown in inert gases.

4. Macroscopic production studies

Fuss *et al*²³⁻²⁵ 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 millijoules of energy at 5-10 kHz repetition rate. For 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 two weeks which ultimately isolated 25 g of total carbon at 50% C-13 enrichment from an overall processing of about 29 kg. For the C-12 case, 4 moles of chlorodifluoromethane was processed in over a period of two weeks to yield CF_2HCl containing C-12 atom fraction of 99.99%.

Based on our experience, we are currently working on the macroscopic separation of carbon isotopes by IR laser chemistry using a pulsed CO₂ laser with the following targets (cf. table 1).

The block diagram in figure 1 gives a general description of the system designed for realizing our objective:

Laser and accessories include the pulsed CO₂ laser source (Macrooptica, Russia) and various optical elements like windows, grating, mirrors, lenses etc., also detectors for energy (GenTec, Canada) and temporal profile measurements (Edinburgh Instruments, UK). The photochemical reactor, which is being indigenously developed, includes Herriott multipass refocusing (MPRF) optics in flow configuration with internal gas blowers for gas circulation during the laser irradiation, control valves, pressure and vacuum transducers etc. Product separator includes a home-made cryogenic distillation set up and a commercial preparative gas chromatograph (Toshniwal Instruments, India) for isolating and purifying the enriched photoproduct from the bulk residual reactants and other side products. Diagnostics include Fourier transform Infrared spectrometer (Nicolet, USA), Analytical gas chromatograph (Shimadzu, Japan), Quadrupole mass spectrometer (VG Elemental, UK). Feed includes gas handling system with purifier etc.

4.1 Laser source

The 50 W pulsed CO₂ laser operates at 10 Hz and gives rise to 5 J energy on 10 P (20) line at 944 cm⁻¹. It is tunable over 70 lines in the 9.0–11.0 μm band region. The laser can operate in both sealed-off and gas flow mode. The temporal profile of the emitted pulse can be varied by adjusting the lasing gas mixture (CO₂, N₂ and He) composition.

Table 1. Macroscopic production of carbon isotopes.

System	Species enriched	Enrichment level	Production rate (total carbon)
Neat CF ₂ HCl	Carbon-13	50%	100 g/year
Neat CF ₂ HCl	Carbon-12	99.99%	400 g/year
Two-stage closed chemical cycle	Carbon-13	Better than 95%	10 g/year

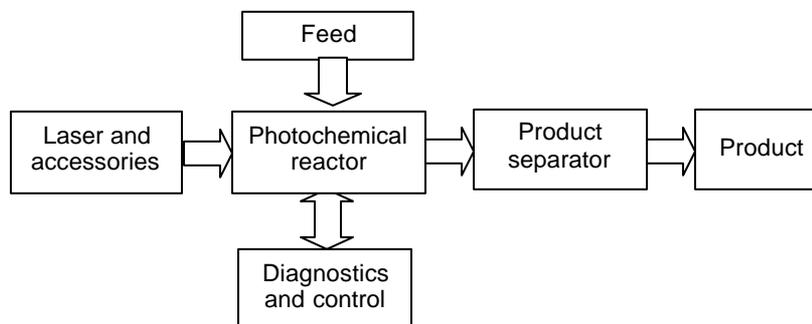


Figure 1. Block diagram of the general schematic.

4.2 Photochemical reactor

The photochemical reactor has a modular structure of three inter connected zones with an overall length of 150 cm. Each module has two compartments, viz. (i) the laser interaction chamber (LIC) and (ii) the gas blower chamber (GBC) which can be decoupled from each other. In each of the GBC, a centrifugal blower is mounted to facilitate a continuous circulation of the gases in the irradiated zone at variable speeds to avoid thermal effects during irradiation. In the absence of such a circulation, there can be a severe selectivity loss in the system. The Herriott type MPRF optics^{26,27} is housed in the LIC for efficient photon utilization and has a stable optical resonator (cf. figure 2) consisting of two coaxial concave mirrors separated by the length of the cell. The laser beam is injected off axially through a small hole near the periphery of one of the mirrors and travels between them in a zigzag manner. With proper design and alignment, every reflection refocuses the beam to the same waist radius in the central plane between the mirrors. The mirror material and its coating should be such that they withstand the hard irradiation conditions in the chemical environment of the photolysis.

4.3 Cryogenic distillation system

In photochemical studies we have to isolate/pre-concentrate the useful end product from the bulk starting material and other side products in gas phase in the post irradiation stage. We have designed and fabricated a cryogenic distillation apparatus²⁸ for the isolation of tetrafluoroethylene (C_2F_4) from chlorodifluoromethane (CF_2HCl). The system has three components viz.: Re-boiler (maintained at $-40^\circ C$), distillation column, and condenser (maintained at $-140^\circ C$).

Experimental conditions for the cryogenic distillation are as follows:

Vacuum: 5×10^{-2} Torr
 Overall volume: 5 litre
 Distillation temperature: $-40^\circ C$ to $-140^\circ C$
 Column height: 70 cm
 Packing material: Dixon rings.

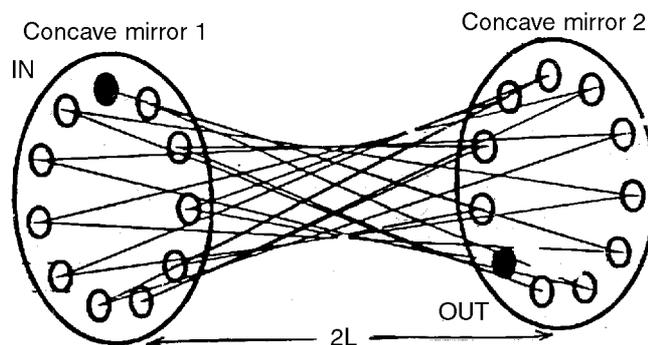


Figure 2. Herriott MPRF optics.

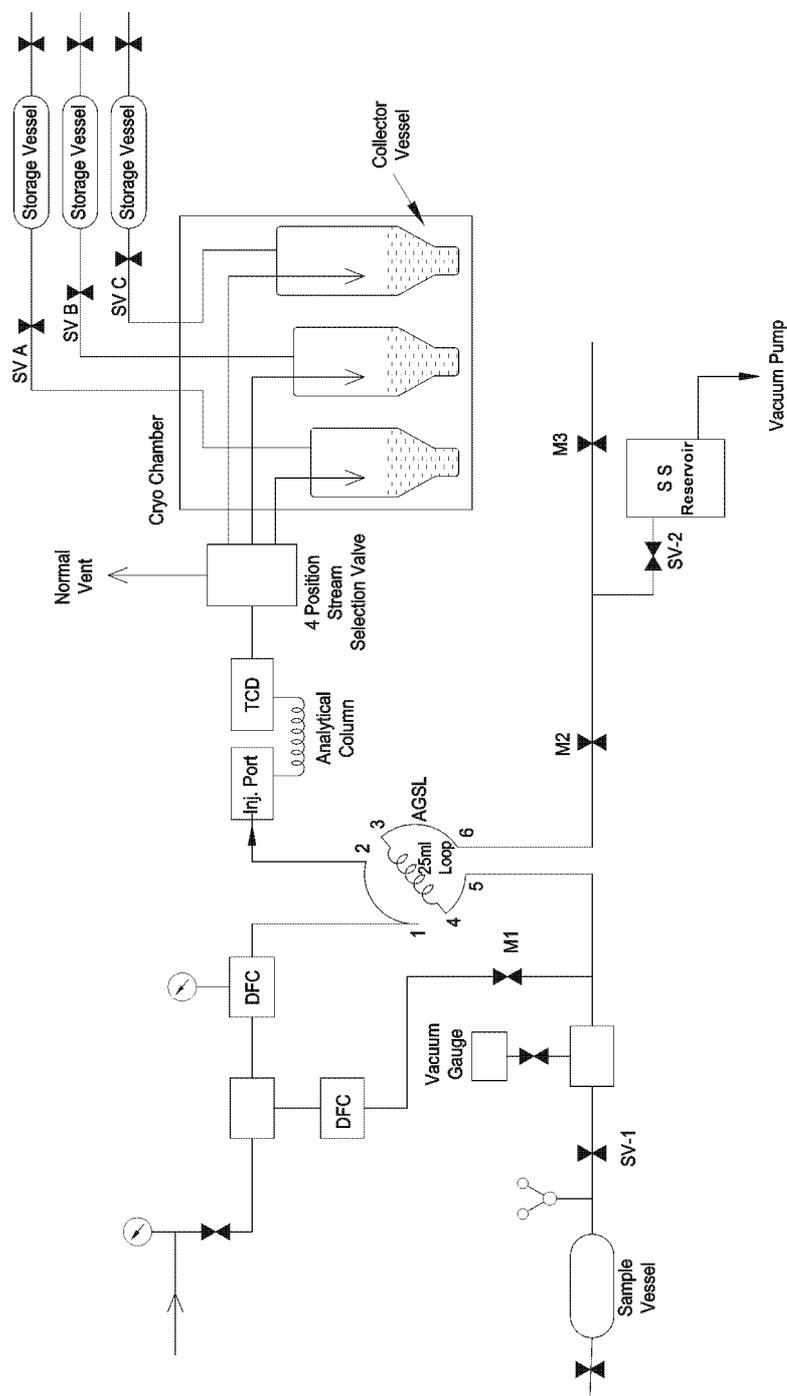


Figure 3. Schematic of the preparative gas chromatograph. SV -1, SV-2: Solenoid valves; SV-A, SV-B, SV-C: Stream selection valve positions; M1, M2, M3 Manually operated valves; TCD: Thermal conductivity detector; DFC: Differential flow controller.

In this temperature range, there is an appreciable vapour pressure difference between C_2F_4 and CF_2HCl facilitating 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 are very important for efficient product separation during the distillation process.

Runs with synthetic mixture samples of C_2F_4 and CF_2HCl have yielded promising results. For example, we could isolate 98.5% pure C_2F_4 after loading the CDS with a sample of CF_2HCl containing about 5% C_2F_4 initial concentration. Starting with an initial value of 1% C_2F_4 in CF_2HCl , we obtained volatile fractions with about 70% C_2F_4 . Further improvement is in progress.

4.4 Preparative gas chromatograph

After pre-concentration, final purification of the enriched product will be done by the preparative gas chromatograph.²⁹ This unit has 8 feet long and ¼ inch diameter Porapak-Q column for separating larger quantities of material compared to an analytical GC. In a single batch, more than 25 ml of the process mixture at atmospheric pressure can be loaded. The equipment has a custom built sample handling system as per our design. Using the combination of a programmable logic controller, auto gas injection valve and a stream selection valve, the process of automatic sampling, injection and fractions separation can be conveniently effected. We have optimized the conditions for a clean separation of the gaseous components using synthetic mixture of C_2F_4 and CF_2HCl . Figure 3 gives a schematic of the set up.

5. Conclusions

This review summarizes the IR laser chemistry involved in the context of carbon isotopes enrichment. It also describes the efforts and strategies being adapted at BARC, India for the separation at macroscopic levels.

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References

1. Coleman D C and Fry B (eds) 1991 *Carbon isotope techniques* (San Diego, CA: Academic Press)
2. Chapman T E, Berger R, Reijngoud D J and Okken A (eds) 1990 *Stable isotopes in pediatric nutritional and metabolic research* (Andover, Hampshire: Intercept)

3. Philips M 1992 *Sci. Am.* **7** 52
4. Koletzko S, Haisch M, Seeboth I, Braden B, Hengels K, Koletzko B and Hering P 1995 *Lancet* **345** 961
5. Lettington A H and Steeds J W 1993 *Philos. Trans. R. Soc. London* **A342** 193
6. Hackett P A 1988 *Laser Chem.* **9** 75
7. Matwiyoff N A, McInteer B B and Mills T R (Summer 1983) *Los Alamos Science* 65
8. Bittenson S and Houston P L 1977 *J. Chem. Phys.* **67** 4819
9. Drouin M, Gauthier M, Pilon R, Hackett P A and Willis C 1978 *Chem. Phys. Lett.* **60** 16
10. Gauthier M, Hackett P A and Willis C 1980 *Chem. Phys.* **45** 39
11. Sarkar S K, Parthasarathy V, Pandey A, Rama Rao K V S and Mittal J P 1981 *Chem. Phys. Lett.* **78** 479
12. Abdushelishvili G I, Avatkov O N, Bagratashvili V N, Baranov V Yu, Bakhtadze A B, Belikhov E P, Vetsko V M, Gverdsiteli I G, Dolzhikov V S, Esadze G G, Kazakov S A, Kolomiiskii Yu R, Letokhov V S, Pigul'skii S V, Pismennyi V D, Ryabov E A and Tkeshlashvili G I 1982 *Sov. J. Quantum Electron.* **12** 459
13. Gauthier M, Cureton C G, Hackett P A and Willis C 1982 *Appl. Phys.* **B28** 43
14. Gauthier M, Outhouse A, Ishikawa Y, Kutschke K O and Hackett P A 1984 *Appl. Phys.* **B35** 173
15. Outhouse A, Lawrence P, Gauthier M and Hackett P A 1985 *Appl. Phys.* **B36** 63
16. Parthasarathy V, van den Bergh H, Kuhne R O and Quack M (unpublished results)
17. Parthasarathy V, van den Bergh H and Quack M (unpublished results)
18. Parthasarathy V, Sarkar S K, Iyer N V, Rama Rao K V S and Mittal J P 1993 *Appl. Phys.* **B56** 321
19. Parthasarathy V, Sarkar S K, Iyer N V, Rama Rao K V S and Mittal J P 1990 Laser isotope separation of carbon-13. A comparative study, BARC Report no. 1524, Bhabha Atomic Research Centre, Trombay, Mumbai
20. Batra A, Sarkar S K and Parthasarathy V 1994 *J. Photochem. Photobiol.* **A83** 193
21. Parthasarathy V, Sethi S, Gantayet L M, Nilaya P, Biswas D J, Iyer N V, Rao K A and Sarkar S K 1997 *J. Photochem. Photobiol.* **A110** 11
22. Parthasarathy V, Nad S, Rao K A and Sarkar S K 1998 *J. Photochem. Photobiol.* **A115** 1
23. Fuss W, Gothel J, Ivanenko M, Schmid W E, Hering P, Kompa K L and Witte K 1994 *Isotopenpraxis Environ. Health Stud.* **30** 199
24. Gothel J, Ivanenko M, Hering P, Fuss W and Kompa K L 1996 *Appl. Phys.* **B62** 329
25. Ivanenko M, Hering P, Bielesch U, Schafer J, Uhlenbusch J, Fuss W and Kompa K L 1997 *Proceedings of Int. Conf. 'Lasers 97'* (New Orleans: USA)
26. Herriott D, Kogelnik H and Kompfner R 1964 *Appl. Opt.* **3** 523
27. Herriott D and Schulte H J 1964 *Appl. Opt.* **4** 883
28. Kale, M R, Sali V A, Nayak A K, Parthasarathy V and Das D 2002 *Proceedings of the National Seminar of Indian Scientific Glass Blowers* (IIT, Chennai)
29. Parthasarathy V, Nayak A K and Sarkar S K 2002 *Proceedings of the 3rd Asian Photochemistry Conference* Mumbai