



## T.1 Efficient macroscopic separation of C-13 isotope using high average power TEA CO<sub>2</sub> laser

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### 1. Introduction

C-13 isotope is found in nature with 1.11% natural abundance. Because of excess mass and non-zero nuclear spin, presence of C-13 can be detected in any carbon compound. These two properties are exploited in medical, environmental and geological science. In environmental and geological studies the change in abundance of C-13 in samples with respect to 1.11% is studied to analyze the environmental and geological changes. However, for medical applications the percentage of C-13 in the carbon compounds should be nearly 99%. The market of C-13 labeled compounds in the study of metabolic pathways, magnetic resonance imaging (MRI) and in determination of complex molecular structures using NMR is increasing. Presently C-13 isotope is separated by conventional technique such as low temperature rectification of CO. The cost of production of C-13 isotope could be reduced by a hybrid technique, in which the initial enrichment up to about 50% is achieved by laser technique and the rest is achieved by conventional technique. Technique to separate the isotopes using laser is known as Laser Isotope Separation (LIS). The laser normally used to separate C-13 isotope is Transversely Excited Atmospheric (TEA) pulsed CO<sub>2</sub> laser. The basic philosophy to separate C-13 isotope using TEA CO<sub>2</sub> laser is selective Infra-Red Multi-Photon Dissociation (IRMPD) of minor C-13 bearing molecules in an ensemble of major C-12 bearing molecules by intense laser pulses resulting in formation of an enriched product.

We have developed a line tunable high average power TEA CO<sub>2</sub> laser and employed it for basic studies on C-13 isotope separation. Freon-22 (CF<sub>2</sub>HCl) is most suitable molecule for C-13 isotope separation. We have designed a novel Linear Multi-Pass Cavity (LMPC) in which the fluence remains constant in each pass.

### 2. Laser isotope separation using TEA CO<sub>2</sub> laser

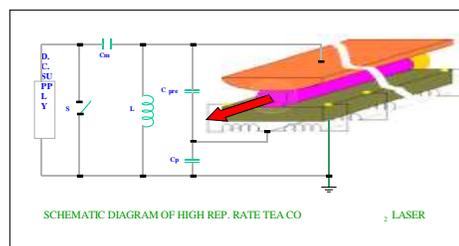
In laser isotope separation process the difference in absorption spectra is exploited. When the monochromatic and tunable laser interacts with an isotopic mixture of molecules, one of the isotopic variant absorbs laser light preferentially while the other variant remains almost untouched. This technique is commonly known as Molecular Laser Isotope Separation (MLIS). This method has been mostly applied for the separation of relatively light isotopes such as H, D, T, B, C,

N, O, Si, S, Cl, Ge, Se and Zr [1, 2]. In MLIS method, a gas mixture with infrared active molecules is irradiated by an intense IR source, such that the desired isotope bearing molecules dissociate preferentially and form a new product. The product is enriched in the desired isotope. The dissociation of infrared active molecules in intense infrared radiation bath is termed as Infra-Red Multi-Photon Dissociation (IRMPD).

Molecules in real world are anharmonic and its vibration energy levels are represented by a ladder whose separation between two consecutive steps keeps on reducing, as we go up the ladder. A molecule will dissociate if it can absorb enough energy from the laser and reaches to its dissociation level. But due to anharmonicity, molecules can't absorb large number of photons of same wavelength and climb up the vibrational ladder and dissociate. However, at high intensities, a molecule climbs the vibrational ladder through non-stationary or virtual states. The life of these states is very small, thus many photons are required in a very small time to facilitate a molecule climb up the vibration ladder and dissociation. This process is known as Multi-Photon Dissociation (MPD).

### 3. High average power UV pre-ionized TEA CO<sub>2</sub> laser

We have developed a high average power TEA CO<sub>2</sub> laser [3]. The laser is based on UV pre-ionized electrical discharge created between a Chang profiled electrode and a plane electrode as shown in fig.T.1.1. This scheme provides high peak current because when same current is flowing in all sparks the mutual inductance in the path is almost zero. Under normal mode operation of TEA CO<sub>2</sub> laser, the stable resonator gives randomly polarized laser pulse at 10P(20) laser line. Laser was made line tunable by employing a grating in the resonator. Laser oscillations could be tuned over several rotation lines in 9.6 and 10.6 mm bands.



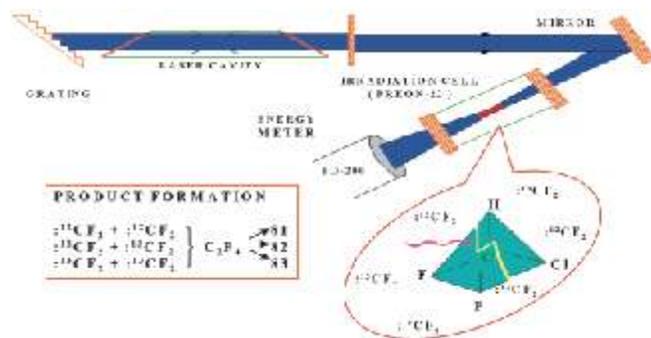
**Fig T. 1.1** Schematic diagram of laser and electrical excitation circuit



In Freon molecule the C-F bond is excited by CO<sub>2</sub> laser wavelengths. Although peak absorption of <sup>13</sup>C-F and <sup>12</sup>C-F differs by 24cm<sup>-1</sup>, there is appreciable overlap in absorption band of two isotopes. Due to this overlap the undesired isotopic species (<sup>12</sup>CF<sub>2</sub>HCl) also get excited at frequencies at which the yield of C-13 is large. Laser line towards red edge of <sup>13</sup>CF<sub>2</sub>HCl absorption curve can be chosen to reduce the yield of undesired isotope (C-12), it also reduces the yield of C-13 isotope. High intensities are required to drive a molecule up in the anharmonic vibration ladder; the high peak power is a primary requirement to dissociate a polyatomic molecule. TEA laser normally emits optical pulse having an initial spike of megawatts of peak power followed by a long tail. While the initial spike is useful for selective dissociation, the tail can totally destroy the selectivity. The reason is that when <sup>13</sup>CF<sub>2</sub>HCl molecules are selectively excited, they also collide with the non-resonant <sup>12</sup>CF<sub>2</sub>HCl molecules. The absorbing energy from the tail of laser pulse will dissociate the excited <sup>12</sup>CF<sub>2</sub>HCl. Eliminating nitrogen from laser gas mixture can produce tail-free pulse in TEA CO<sub>2</sub> laser, but it drastically reduces the laser efficiency. We produced laser pulse of about 130ns duration in an optimized laser gas mixture with CO<sub>2</sub>:N<sub>2</sub>:He::140:30:630 mbar.

#### 4. C-13 isotope separation studies in small cell

Experiments on selective dissociation of CF<sub>2</sub>HCl were carried out in a small cell of volume 100 cm<sup>3</sup>. Since the unfocused laser beam fluence is much smaller than required for MPD, the beam is focused with a concave mirror of 50cm radius of curvature (ROC) kept at an angle of about 10.5°. The schematic of laser and irradiation cell is shown in fig.T.1.2.



**Fig T.1.2** Schematic diagram of line tunable TEA CO<sub>2</sub> laser and small irradiation cell

#### 5. IRMPD of Freon-22

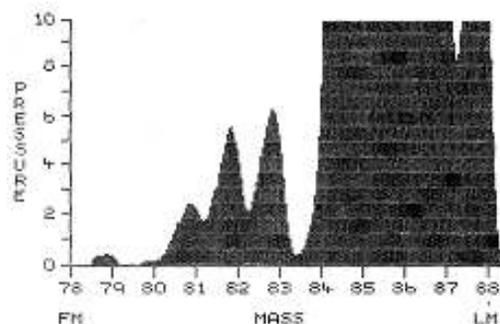
The <sup>13</sup>CF<sub>2</sub>HCl molecules can be selectively dissociated by an appropriate choice of laser line in 9P band of CO<sub>2</sub> emission spectrum. The dissociation process and product formation are:



Ideally <sup>13</sup>CF<sub>2</sub> radicals should be produced but for appreciable yield of <sup>13</sup>CF<sub>2</sub> the chosen laser line also produces <sup>12</sup>CF<sub>2</sub> radicals. This leads to formation of product C<sub>2</sub>F<sub>4</sub> that has some percentage of C-12 atoms. The enrichment factor b is expressed as:

$$b = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{prod.}}}{(^{13}\text{C}/^{12}\text{C})_{\text{react.}}}$$

For enrichment factor b=100, the C-13 atoms in C<sub>2</sub>F<sub>4</sub> is nearly 50%. Our goal is to produce a product with enrichment factor b=100. The enrichment factor in the product is measured with the help of quadrupole mass analyzer (QMA). A plot of an enriched product is given in fig.T.1.3.



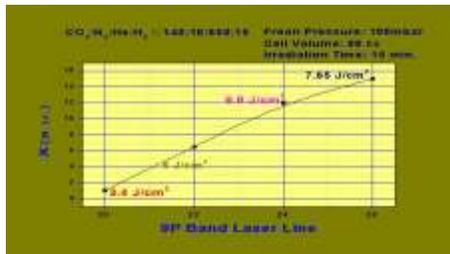
**Fig T.1.3** Mass plot of C<sub>2</sub>F<sub>3</sub><sup>+</sup> ions produced in QMA with an enriched C<sub>2</sub>F<sub>4</sub> sample

#### 6. Maximization of yield of C-13 isotope

One of the important issues is to increase the enrichment efficiency. In literature C-13 isotope separation studies at various lines from 9P(20) to 9P(30) have been reported. We have carried out extensive experiments on C-13 separation at various laser lines under same conditions to resolve the issue [4]. We found optimum pressure 100mbar of Freon, for maximum selectivity, and the measurements are done at 6Hz laser repetition rate. Our main objective was to find out the laser line at which the yield was highest for 50% enriched product (i.e. b=100). The laser lines used for irradiation were 9P(20) to 9P(26). The amount of 50%



enriched  $C_2F_4$  produced at different laser lines and its corresponding optimum fluence is plotted in fig. T.1.4.



**Fig T.1.4** Amount of 50% enriched  $C_2F_4$  versus laser line

We see that 9P(26) laser line is better compared to blue shifted lines such as 9P(22) because the laser energy required at 9P(26) is just 1.5 times of the energy required at 9P(22) but the amount of enriched product is more than double. The reason for higher enrichment efficiency is due to higher operating fluence at red shifted lines for desired enrichment in the product. It is not very clear what happens at high fluence value. To resolve this we studied the dependence of yield of C-13 i.e.  $^{13}Y$  (ratio of number of  $^{13}CF_2HCl$  dissociated to number of  $^{13}CF_2HCl$  irradiated) on fluence ( $f$ ). In multi-photon dissociation one would expect

$^{13}Y \propto f^g$ , Where  $g$  is the non-linearity factor.

Yield of C-13 isotope  $^{13}Y$  was plotted against fluence ( $f$ ) in a semi-log graph and  $g$  was obtained from the slope.

The value of  $g$  at 9P(22) and 9P(26) was 3.85 and 1.99 respectively. Due to lower value of  $g$ , the reaction volume in case 9P(26) is large compared to that at 9P(22). This high reaction volume at 9P(26) laser lines gives higher enrichment efficiency. Another advantage of irradiation at 9P(26) laser line is due to its smaller linear absorption coefficient in Freon as compared to blue shifted lines. We have measured the linear absorption coefficient at 9P(22) and 9P(26) laser lines and their value are 0.25%/cm and 0.147%/cm respectively. Due to small value of total absorption coefficient, only a small fraction of laser energy is utilized in a single pass. To utilize the laser energy efficiently, longer path length is required and this can be achieved in a suitably designed multi-pass cell.

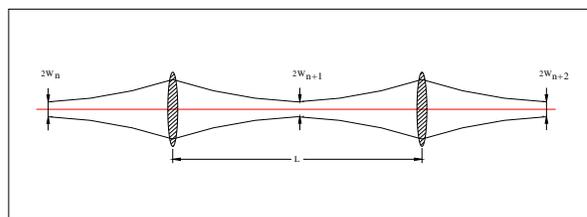
## 7. Multi-pass cell

Herriott multi-pass cell has been used for refocusing of the laser energy to generate multiple focal volumes where MPD can take place [5]. The Herriott cell has several advantages but suffers from the following limitations:

- The focal spot size in each pass is the same.
- The focal spot size in each pass is difficult to control individually.

The optical equivalent of a section of a typical Herriott cell is represented by a combination of lenses as shown in fig.T.1.5.

The  $W_n$ ,  $W_{n+1}$  and  $W_{n+2}$  are the minimum Gaussian beam waist at three consecutive locations. Using the ABCD matrix for Gaussian beam propagation, the separation between two lenses  $L$ , can be given by eq. (1) when the beam waist is reducing by factor  $d$  in subsequent passes.



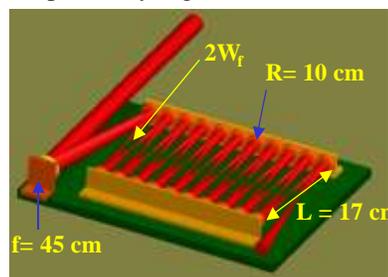
**Fig T.1.5** Optical equivalent of a section of typical multi-pass cell

$$L = f \frac{\frac{d}{e}}{\frac{e}{d}} + d \sqrt{\frac{\frac{d}{e}}{\frac{e}{d}} \left[ 1 - \frac{d^2 z_r^2}{f^2} \right]} + \sqrt{\frac{\frac{d}{e}}{\frac{e}{d}} \left[ 1 - \frac{d^4 z_r^2}{f^2} \right]} \quad (1)$$

Where,  $d = \frac{W_{n+1}}{W_n} = \frac{W_{n+2}}{W_{n+1}}$ ,  $f$  = focal length of lens,

$$z_r = \frac{\rho W_n^2}{l} \quad (\text{Rayleigh range})$$

It is obvious from eq.1 that in a Herriott cell, where  $L$  is same for all passes, the focal spot size  $W_n$  can't be changed. If the focal spot size needs to be gradually reduced ( $d < 1$ ),  $L$  has to gradually increase with repeated passes. We have designed a new multi-pass cavity termed as Linear Multi-Pass Cavity (LMPC) [6] in which the mirror separation for each pass can be adjusted independently (fig T.1.6a).



**Fig T.1.6a** Schematic diagram of LMPC



**Fig T.1.6b** Simulated beam path and multiple focal volumes produced by He-Ne laser.

The imaging scheme in LMPC tested by launching a He-Ne laser beam (fig.T.1.6b). It consists of 10 pairs of similar mirrors of 10.0 cm ROC placed in two rows facing each other. These are the imaging mirrors used to relay the image formed by the first mirror of large ROC (45 cm). As shown in fig.T.1.6a, the unfocussed beam from the laser is incident on the first mirror. This mirror along with the plane mirror (to fold the beam) focuses the beam in front of the first imaging mirror. This focal spot serves as an object for mirror labeled '1' which forms the image in front of mirror labeled '2'. The focal spot in each pass can be reduced in proportion to reduction in energy per pass, thus we can maintain the fluence constant in all focal zones.

Irradiation of Freon gas was carried out in LMPC in two modes, namely, constant focal spot case and gradually reducing focal spot case to evaluate the advantage of LMPC. It was observed that with the same energy, the reaction volume offered by constant fluence (or gradually reducing focal spot case) was nearly 1.5 times more than reducing fluence (or constant focal spot case). The amount of C-13 produced was also more, thus, the energy utilization factor had significantly improved in LMPC.

## 8. Macroscopic production of C-13 isotope

For macroscopic production of C-13 isotope, irradiation of Freon gas has to be done at high laser repetition rate. The selectivity of excitation is lost if the temperature of gas in reaction volume rises. We therefore designed a large irradiation cell with 110-liter volume incorporated with a magnetic coupled tangential blower to flow the gas in the reaction zone and the LMPC was placed in it (fig.T.1.7). Irradiation of Freon gas at 100 mbar was carried out at 9P(26) laser line and at 100Hz for 100 minutes. The TEA CO<sub>2</sub> laser was operated in purging mode. In this mode fresh laser gas mixture is continuously purged in and contaminated laser gas mixture is taken out to control the accumulation of oxygen for stable operation of gas discharge.



**Fig T.1.7** TEA CO<sub>2</sub> laser and large irradiation cell of 110 liter

We produced C-13 isotope at a rate of 15 mg/hr in the form of ~ 50% enriched C<sub>2</sub>F<sub>4</sub>. The estimated enrichment efficiency was  $1.73 \times 10^7$  gm per joule of laser energy, which is one of the highest reported values.

## 9. Conclusions

A high average power, line tunable, UV pre-ionized TEA CO<sub>2</sub> laser has been developed for laser based separation of C-13 isotope. For efficient separation of C-13 isotope, irradiation of Freon gas by laser lines towards red edge of <sup>13</sup>CF<sub>2</sub>HCl absorption curve were found more suitable. In the present study, 9P(26) laser line gave highest enrichment efficiency as compared to 9P(20) – 9P(24) laser lines. For efficient utilization of laser energy, LMPC has been designed which has a unique feature of maintaining fluence constant in each pass. Freon gas could be irradiated with optimum fluence in each pass, thus enhancing the enrichment efficiency (highest reported) as well as ensuring efficient utilization of laser energy.

## References

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